Aalto University
School of Chemical
Technology

School of Chemical Technology
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Hongliang Zheng

PRODUCTION OF FIBRILLATED CELLULOSE MATERIALS - EFFECTS OF PRETREATMENTS AND REFINING STRATEGY ON PULP PROPERTIES

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Supervisor	Professor Thaddeus Maloney
Instructor	M.Sc. Juuso Rantanen

Aalto University
School of Chemical Technology

Aalto University, P.O. BOX 11000, 00076 AALTO
www.aalto.fi

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Author Hongliang Zheng

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Thesis advisor M.Sc. Juuso Rantanen

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Abstract

The aim of this work was to manipulate the sub-cell wall swelling of wood fibers and then refining in a conventional refiner to demonstrate the possibility of producing useful fibrillated cellulose product. The swelling was changed by two different pretreatments: enzymatic hydrolysis and anionic polymer adsorption. In addition, a modified Valley beater was tested to study the effect of fiber cutting as a pretreatment.

Both pretreatment methods: cellulase hydrolysis and anionic polymer adsorption showed potential on manipulating the swelling properties of cellulose fiber and facilitating disintegration of pulp during refining. The swelling results showed it is possible to increase internal fibrillation of fibers without increasing the fiber swelling by using both methods, especially by cellulase hydrolysis. The sharp edge bars of modified Valley beater mainly shorten the fiber rather than fibrillate it compared with standard one.

Keywords Fibrillated cellulose, cellulase, PAA, Valley beater, swelling properties, surface area

Table of Contents

1. Introduction

Interest in microfibrillated cellulose (MFC) has been increasing exponentially. Microfibrillated cellulose is a material composed of nanosized cellulose fibrils with diameter in range of 10-40 nm and length of several micrometers (1). The aspect ratio of MFC is normally about 100-150. Due to their abundance, high strength and stiffness and biodegradability, nano-scale cellulose fiber materials serve as promising raw material for bio-nanocomposite production.

The development of microfibrillated cellulose was pioneered by Turbak et al. (2) and Herrick et al. (3). They presented a gel-like material, which they named microfibrillated cellulose (MFC). It was produced by treating wood based cellulose fiber suspensions with a high-pressure homogenizer. Several mechanical treatments have been developed to produce MFC since then. Homogenizer, microfluidizer and grinder are the most common devices used among them. However, each of the above mechanical treatments requires high energy consumption. For instance, the energy consumption of homogenizer process reaches as high as 70,000 kWh/t (4). The energy consumption is the main drawback of producing MFC in large scale, which held back the commercial success of MFC products.

Recently, especially after year 2005, growing interest in renewable nanomaterial resulted in a revival of MFC research and many research groups were working with this material around the world. Most of those researches were focused on the characterization and applications of MFC rather than the production processes. However, several publications considered the mechanical treatment and pre-treatment of MFC production. At this point, it is hard to judge the best solution to produce MFC. The existing studies, however, indicate that the combination of pre-treatment and mechanical treatment is a promising solution to obtain cost-efficiency.

The aim of this thesis is manipulating the sub-cell wall swelling of wood fibers and then refining in a conventional refiner to testify the possibility of producing fibrillated cellulose product.

The swelling will be changed by two different pretreatments: enzymatic hydrolysis and anionic polymer adsorption. In addition, a modified Valley beater was tested to verify the possibility of improving the procedure and reducing energy consumption.

2. Review of research

2.1 Cellulose and nanocellulose

2.1.1 Cellulose

Cellulose is the most abundant organic polymer on earth (5), mainly found in wood, cotton, hemp and other plant-based materials. It is considered as an almost inexhaustible source of raw material for the increasing demand of environment friendly and biocompatible products. As a renewable material, cellulose and its derivatives have been widely studied, focusing on their biological, chemical, and mechanical properties. The materials based on cellulose and its derivate have wide applications, such as food and pharmaceutical, paper and board production, and biofuel.

Since it was discovered in 1883, the properties of cellulose have been intensively studied. Figure 1 shows the molecular structure of cellulose as a carbohydrate polymer consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units (6). The amount of repeated glucose units, the degree of polymerization (DP) varies with the origin and treatment of the raw material. Cotton and other plant fibers have DP value in the 10000-15000 range, and the DP values of wood pulp are typically 300-1700 (5). The molecular structure of cellulose is important as it explains the characteristic properties of cellulose, such as hydrophilicity, biodegradability and high functionality.

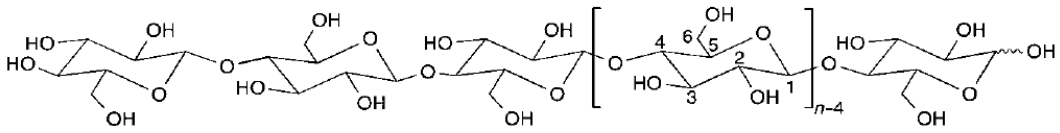

Figure 1 Molecular structure of cellulose (7).

There are four different polymorphs of cellulose (Figure 2). The crystal structure of native cellulose (cellulose I) is present in two different crystalline modifications (I_α and I_β), which can be found alongside each

other; the I_α / I_β ratio depends on the origin of the cellulose. Apart from cellulose I, cellulose may exist in other crystal structure (cellulose II, III, IV), of which cellulose II is the most stable from (8).

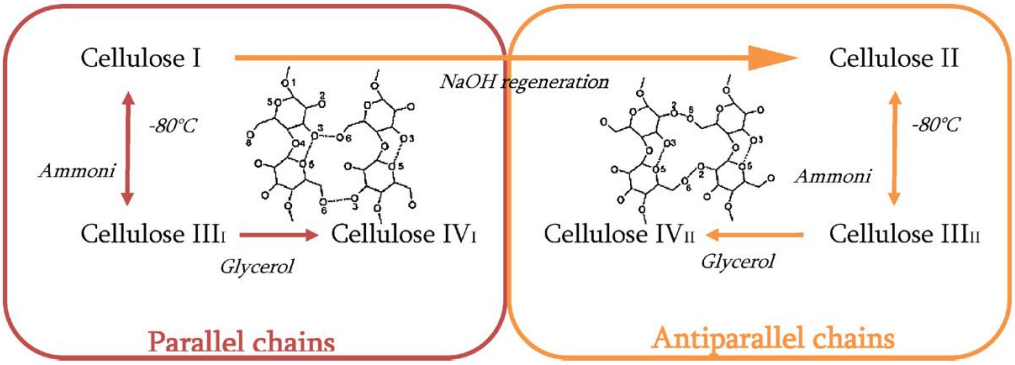

Figure 2 Polymorphs of cellulose and the main steps to obtain them (9).

2.1.2 Nanocellulose

The production of nano-scale cellulose fibers and their application in composite materials had gained increasing attention recently. Due to their abundance, high strength and stiffness and biodegradability, nano-scale cellulose fiber materials (e.g., microfibril, microfibrillated cellulose, and cellulose nanocrystals) serve as promising raw material for bio-nanocomposite production.

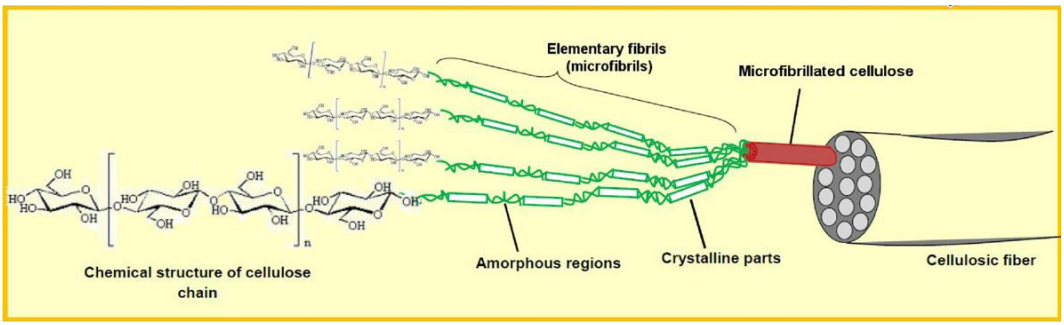

Figure 3 The hierarchical structure of a cellulosic fiber from cellulose polymer to elementary fibril to microfibril and a fiber (9).

The microfibrils are formed during the cellulose biosynthesis in higher plants. Depending on their origin, the microfibril diameter may vary. It is

typically in the range of 2-10 nm with the length of several tens of microns (10) .

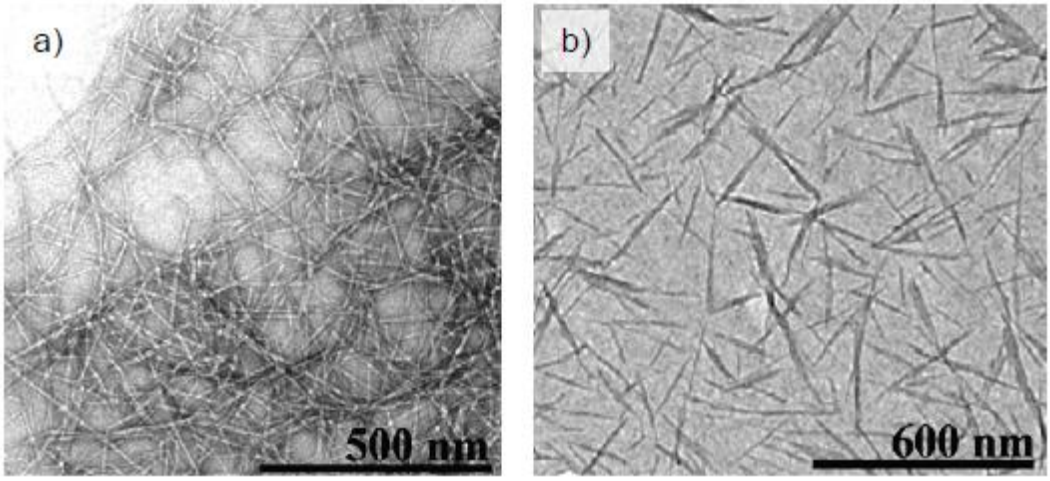

Figure 4 Transmission electron micrographs of a) MFC, b) NCC (11).

However, the two main types of nanocellulose are: cellulose nanocrystals (CNC) and microfibrillated cellulose (MFC) as showed in Figure 4. Table 1 shows the size difference of microfibrillated cellulose, and cellulose nanocrystals. Different steps are involved in the preparation of those two types of nanocellulose.

Table 1 Nanocellulose dimension (1, 10, 12).

Cellulose structure	Diameter (nm)	Length (nm)	Aspect ratio (L/d)
Microfibril	2-10	>10000	>1000
Microfibrillated cellulose (MFC)	10-40	>1000	100-150
Cellulose nanocrystals (CNC)	2-10	100-600	10-100

Cellulose nanocrystals

Many terms are used to refer to cellulose nanocrystals: nanocrystalline cellulose, microcrystals, nanoparticles, microfibrils. Hereafter, it is called “cellulose nanocrystals (CNC)”

Cellulose nanocrystals are rigid rod-like crystals with diameter in range of 2-10 nm and length of 100-600 nm (1) derived from acid hydrolysis of native cellulose. Native cellulose consists of amorphous and crystalline regions. Under controlled acid situation, the amorphous regions surrounding and embedded within the cellulose microfibrils disrupt because low resistance of acid, which release the individual crystallites. The properties of CNC depend on various factors: the origin of cellulose microfibrils, reaction time and temperature and types of acid used for hydrolysis (13).

A typical preparation of CNC proposed by Bondeson et al. (14), CNC can be produced from microcrystalline cellulose with a sulfuric acid concentration of 63.5% (w/w) and a reaction time of 130 min. The diameter of final product is smaller than 10 nm, and the length is ranging between 200 and 400 nm, with a 30% yield of the initial weight.

Due to its structure, chemical reaction can be easily conducted on the surface of CNC because an abundance of hydroxyl groups. Various chemical modifications of CNC have been studied, such as TEMPO-mediated oxidation, cationization, esterification, silyation, polymer crafting, and noncovalent surface chemical modifications (15). Most of those researches focused on the improvement of its dispensability and compatibility in different solvents.

The modification of CNC is gaining increasing attention because the wide potential applications of modified CNC in various industrial sectors, including nanocomposites, biomedical, personal care. It is been reported CNC has its advantages for nanocomposite processing due to the outstanding thermal and mechanical properties. Besides, it can also be used in drug delivery, protein immobilization and metallic reaction template (13).

Microfibrillated cellulose

Many terms are used to refer to microfibrillated cellulose: cellulose microfibril, microfibrillar cellulose, and nanofibrillated cellulose. Hereafter, it is called “microfibrillated cellulose (MFC)”

Microfibrillated cellulose is a material composed of nanosized cellulose fibrils with diameter in range of 10-40 nm and length of several micrometers (1). The aspect ratio of MFC is normally about 100-150. More information about the characterization and applications of MFC will be presented in the following sections.

The development of microfibrillated cellulose was pioneered by Turbak et al. (2) and Herrick et al. (3). They presented a gel-like material, which they named microfibrillated cellulose (MFC). It was produced by treating wood based cellulose fiber suspensions with a high-pressure homogenizer. Followed by the work of Turbak and Herrick, MFC as a new material was studied by Lindström et al. (16), who were trying to utilize this material as a wet-end additive to promote dry strength of paper production.

However, the research was stagnant at that point because two main challenges. Frist, the fibers obstructed the homogenizer, which resulted in frequent stops of the device for cleaning. Second, the process of preparation requires large amount of energy, which was approximately 27000 kWh/ton (16). These two challenges resulted in high cost of the end product and held back its commercial success. Therefore, few studies were present for a long time.

Recently, especially after year 2005, growing interest in renewable nanomaterial resulted in a revival of MFC research and many research groups were working with this material around the world. Most of those researches were focused on the characterization and applications of MFC rather than the production processes. However, several publications studied the mechanical treatment and pre-treatment of MFC production. At this point, it is hard to judge the best solution to produce MFC. The

existing studies, however, indicate that the combination of pre-treatment and mechanical treatment is a promising solution to obtain cost-efficiency.

Very recently, an increasing number of industrial companies such as Stora Enso, UPM, Innventia, Borregaard, Oji Paper and Nippon Paper announced their semi-commercial production line of MFC. Moreover, several European research projects are focusing on the scaling up of MFC production and new applications.

2.2 Production of microfibrillated cellulose

Microfibrillated cellulose can be produced from various cellulosic materials. Bleached Kraft pulp and bleached sulfite pulp are two most used starting materials to produce MFC. However, agriculture crops and their byproducts (17), sugar beet pulp (18), bagasse (19), sisal (20) also have been studied as raw materials to produce MFC.

The production of MFC by fibrillation of cellulose fibers into nano-scale particles requires intensive mechanical treatment. However, several pre-treatments are also applied before mechanical treatments to obtain fibers that are less stiff and cohesive, thus to reduce energy consumption.

2.2.1 Pre-treatments

Alkaline pretreatment

Several researchers have performed alkaline pretreatment before mechanical processing in order to disrupt the lignin structure of fiber (21-23). However, the alkaline treatment needs to be well controlled on the surface of fiber to avoid degradation of cellulose.

Enzyme pretreatment

Various methods have been used to increase the reactivity of dissolving pulps. Use of cellulose degrading enzymes, cellulase, is an interesting method among them. Henriksson (24) studied the mechanism of cellulase and proposed that four functional types of enzymes are required for efficient cellulose degradation. A-type enzyme mainly degrades cellulose chain from the reducing end and releases cellobiose, while B-type enzyme

degrades the cellulose chain from the non-reducing end. C-type enzyme disrupts the cellulose chain. D-type enzyme mildly absorb to crystalline cellulose via a special cellulose binding domain. Different types of enzyme cooperate in a complicated way to degrade cellulose, but they can be highly specifically modificated.

Based on the mechanism of enzymes, several researchers combined the enzyme treatment with mechanical treatment to obtain MFC. Janardhnan S (25) performed enzyme treatment with OS1, a fungi isolated from Dutch disease, when producing MFC. Although Fungi OS1 is mild with cellulose, the results showed lower diameter and improving yield. Pääkkö et al. (26) used enzyme treatment with endoglucanase before passing the pulp through microfluidizer. The result shows a well-controlled diameter of MFC and a significant reduction in energy consumption. Moreover, the MFC with enzyme treatment shows a more favorable structure. López-Rubio (27) and Svagan (28) also combined enzyme pre-treatment with mechanical treatment to obtain MFC. They utilized a four-step process: a normal refining step with Escher-Wyss refiner followed by enzyme treatment with mono component endoglucanase, a second refining step and finally put the pulp through a high-pressure microfluidizer.

Henriksson (29) designed a more comprehensive experiment, where he compared non-pretreated MFC, enzyme pretreated MFC and strong hydrolysis treated MFC. A Gaulin homogenizer was utilized for mechanical treatment. The results showed that enzyme hydrolysis is much milder than acid hydrolysis, which leads to selective hydrolysis of the non-crystalline cellulose. The enzyme pretreated MFC has a lower fibril diameter and increasing amount of fines content. Siqueira (30) studied the impact of enzyme pre- and post- treatment on MFC production. Two kinds of enzymes (exoglucanase and endoglucanase) were used at different concentrations. The result showed that enzyme treatment seems to be a very promising method for MFC production.

Oxidation pretreatment

TEMPO mediated oxidation is a common pretreatment before mechanical processing to produce MFC. It is a promising method for surface modification of native cellulose, by which carboxylate and aldehyde functional groups can be introduced into solid native cellulose under aqueous and mild conditions (31-37) . Another remarkable advantage is significant reduction in the energy consumption compared with non-pretreatment through a high-pressure homogenizer. It has been reported that the energy consumption is decreased from 700 MJ/kg to 7 MJ/kg when producing MFC (38, 39).

Saito (33) performed 2, 2, 6, 6-tetramethylpiperidine-l-oxyl (TEMPO) and NaBr at pH 10-11 at room temperature in a Waring-blender before mechanical treatment. Two kinds of product can be obtained depending on the starting materials. When native celluloses are applied, the initial fibrous morphology is almost maintained after TEMPO-mediated oxidation (38, 39). The oxidation only happened on the surface of microfibrils and leads to negative charge, which was easing fibrillation. On the other hand, if regenerated and mercerized celluloses are applied, water soluble β-1, 4-linked polyglucuronic acid sodium salt with a homogeneous chemical structure can be obtained as the oxidation product (40, 41). A similar process is applied by Isogai et al. (38). The principle behind the pretreatment is the same, but they replaced the NaBr with NaClO, changed the primary oxidant from NaClO to $NaClO_2$, and performed the whole procedure at pH 7.

Besides that, Isogai A. (38) and Isogai T. (39) also developed TEMPO electro-mediated pretreatment to oxidize the C6-primary hydroxyls of cellulose. Two new systems were introduced, electro-mediated oxidation with TEMPO at pH 10, and 4-acetamido-TEMPO at pH 6. The yield is more than 80%, which is quite high. However, the time for oxidation is longer than in previous two methods. Another advantage is that this method preserves the main characteristics of TEMPO-oxidated MFC from bleached softwood Kraft pulp.

Carboxymethylation and acetylation pretreatment

Recent research shows that carboxymethylation and acetylation pretreatment can increase the anionic charges on the surface of MFC by introducing carboxyl groups.

Aulin et al. (42) performed carboxymethylation pretreatment before mechanical treatment and compared with non-pretreated MFC. The result shows that the fibrils are highly charged and easier to liberate after carboxymethylation pretreatment. Another remarkable advantage is that this pretreatment is significantly reducing the energy consumption from 5.5 MWh/t to 2.2 MWh/t per pass through the microfludizer (43).

2.2.2 Mechanical treatments

Several mechanical treatments can be used in the production of MFC. Homogenizer, microfluidizer and grinder are the most common devices used among them. Figure 5 demonstrate the basic principles of these three different methods.

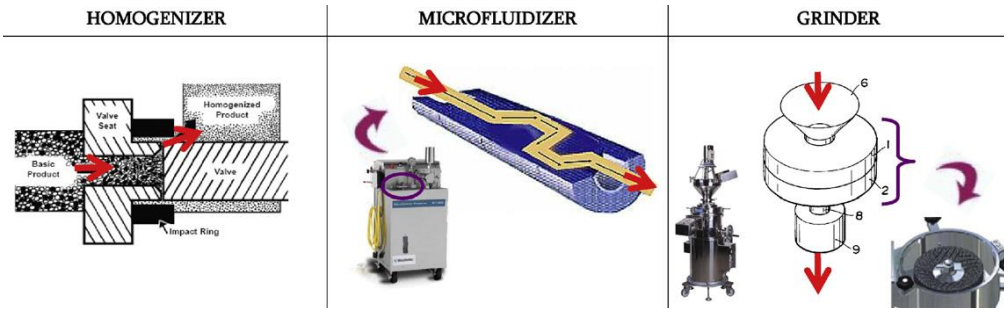

Figure 5 The most applied mechanical treatment processes used in MFC production: the homogenizer, the microfluidizer and the grinder (9).

Homogenizer and microfludizer

A method for producing MFC was first introduced by Herrick (3) and Turbak (2) with a Gaulin homogenizer. Nowadays, the production of MFC usually consists of a mechanical refining and homogenizing process steps (26, 44, 45). For the refining step, a disk refiner is involved. The pulp is forced through a gap between rotor and stator disks to increase the bonding potential by modifying the morphology and size of fibers. This

results in external fibrillation of fibers by peeling off P and S1 layers and exposing S2 layer of fibers. Then the pulp is fed through a spring-loaded valve under a high pressure. The fiber is subjected to a large fluctuating pressure under high shearing force because the valve is rapidly opened and closed, which leads to a high degree of fibrillation of cellulose fibers (46).

Zimmermann (47), López-Rubio (27), Siqueira (48) reported the mechanical treatment using a microfluizer in the homogenisation step, in which the pulp is fed through thin z-shape chamber (the diameter of the chamber is normally 200-400 um) under high pressure (~2000bar). This method provides a more uniformly sized fibers than homogenizer and the diameter of fibril is usually 20-100 nm with length of several tens of micrometers.

However, both homogenizer and microfludizer treatment require the pulp to pass through several cycles (normally 10-30 cycles) to get desired MFC grade, which increases energy consumption. Another limitation is that this kind of device is not ideal for scaling-up to industrial production.

Cryocrushing

Cryocrushing is a rarely used method for producing MFC in which fibers are frozen using liquid nitrogen and mechanical crushing is then applied (49). Alemdar et al. (50) extracted MFC from wheat straw and soy hulls with this method and they claim that almost 60% of the nanofibers had a diameter of 30-40 nm with length of several thousand nanometers. Bhatnagar A. (51) obtained MFC with a diameter of 5-80 nm by performing cryocrushing on flax, hemp, and rutabaga fibers. Wang combined cryocrushing with a high pressure fibrillation process to obtain MFC from soybean stock (52, 53). Cryocrushing is often applied on agriculture crops to produce MFC.

Electrospinning

MFC can also be produced by electrospinning treatment, in which regenerated cellulose is obtained. A few studies have been carried out on this method (54-56). Regenerated cellulose (cellulose II) was obtained with this method.

Grinding

Another frequently used mechanical treatment is grinding, and Masuko Ultra-fine friction grinder is a typical grinding device for this treatment. The cellulose is fed between a static grind stone and a rotating stone rotating at ~1500 rpm, which disrupts the cell wall structure and hydrogen bonds with the shearing force generated by the grinding stone.

Taniguchi et al. (57) obtained MFC with a diameter of 20-90 nm with a super-grinding procedure. Iwamoto and Nakagaito (58, 59) applied 10 repetitions of grinding treatment to obtain a uniform MFC with diameter of 50-100 nm. Iwamoto (59) studied the impact of number of passes through a grinding device on the morphology of MFC. The result shows that during the first one to three passes, most of the fibers became sub-micron-sized and nano-sized fibers, and at five passes, most of fibers become nano-sized fibers. With higher passes through the grinder, no significant change was observed in the morphology of fibers.

Compared with homogenizer and microfludizer treatment, the grinding treatment requires less passes to obtain MFC, however, the microfludizer shortens the chain length more than grinder (59).

2.2.3 Energy consumption

Each of the mentioned mechanical treatments requires high energy consumption. For instance, the energy consumption of homogenizer process reaches as high as 70,000 kWh/t (4). The energy consumption is the main drawback of producing MFC in large scale, which held back the commercial success of MFC products. Therefore, reducing the processing energy requirement is one of the most important requisites to produce MFC on an industrial scale.

Spence et al. (60) conducted a comprehensive study of the energy consumption and physical properties of MFC produced by different processing methods. For bleached and unbleached Kraft hardwood pulps, they compared the consumption as a function of the mechanical treatment, the number of passes, the pressure, and the speed. Their research has shown that compared to homogenization, microfludization with a refining pretreatment and the micro-grinding of wood fibers are production methods which require less energy and produce MFC films with better mechanical properties. Production of MFCs with a homogenizer resulted in microfibrils with the highest specific surface area and films with the lowest water vapor transmission rate. In addition, films produced by a microfluidizer and a grinder presented superior physical, optical, and water interaction properties, which suggests that these materials could be produced in a more economical way for packaging applications.

The development of disintegration methods that are less energy-consumption also becomes a priority in industrialization of MFC production. Thus, different pretreatments were used to reduce the energy consumption. On the other hand, new equipment is being studied and developed in order to obtain MFC with low energy consumption or via a faster process.

2.3 Properties and characterization of microfibrillated cellulose

2.3.1 Morphology

Various techniques have been used to characterize MFC morphology, such as scanning electron microscopy (SEM) and field-emission scanning electron microscopy (FE-SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), wide-angle X-ray scattering (WAXS) and solid state 13C cross-polarization magic angle spinning (CPMAS) NMR spectroscopy.

Depending upon the manufacturing process and the nature of cellulose source, MFC displays similar morphologies but various dimension scopes. The typical dimensions of MFC are 10-40 nm in width and several

micrometers in length. However, the length is estimation and it is more difficult to determine fibril length because of entanglements and difficulties in identifying the individual fibril. All researchers estimate the length of MFC within several micrometers.

Iwamoto et al. (59) obtained MFC of 20-50 nm wide with 15 passes through a non-treatment grinding process. With carboxymethylated pretreatment followed by microfluidizer process, Aulin et al. (42) obtained MFC with 10-15 nm in width. Saito and Nishiyama (33) reported 5 nm wide MFC was obtained with TEMPO oxidation pretreatment. Following enzymatic pretreatment, MFC with diameter of 20-30 nm was obtained from sulfite softwood pulp.

It is obvious that different pre-treatments and mechanical processes have a huge impact on the morphology of MFC. However, it is not accurate to compare those figures directly since researchers used different raw materials. The origin of cellulose fibers, the content of lignin, hemicellulose, and other characteristics all have different influence on the morphology of final products.

Alemdar et al. (50) reported the width of MFC obtained from straw and soy hulls are 10-80 nm and 20-120 nm, respectively. Some researcher also measured the width of MFC obtained from sisal, carrots, and beet pulp, which were 20-65 nm, 3-36 nm, and 30-100 nm respectively (8, 30, 61).

It has been reported that higher hemicellulose content result in a smaller nano fibril aggregation size (62-67), and the presence of hemicellulose in MFC pulp can facilitate nanofibrillation and improve the physical properties of nanocomposites (66). However, with lignin-containing pulp, the size of MFC obtained was larger, regardless of the origin (68).

2.3.2 Degree of polymerization

To measure the degree of polymerization of MFC, researchers normally calculated the average DP from viscosity by using the Mark-Houwink equation (59, 69). The DP of sulfite pulp is around 1200-1400, while the

DP of MFC produced from sulfite pulp is 825 (69), which normally is about 30-50% decrease (29). It has also been reported that degree of polymerization is highly correlated with the aspect ratio of the nanofibers. High cellulose DP is desirable for MFC since this is correlated with increased nanofiber tensile strength (29). Iwamoto (66) reported an elastic modulus of 145 GPa for a single TEMPO-oxidized MFC nanofiber, while the elastic modulus of a perfect crystal of native cellulose is estimated 130-250 GPa (47).

2.3.3 Degree of crystallinity

Since MFC is composed of both crystalline and amorphous regions, knowing the degree of crystallinity and crystallite size could be beneficial to understand the properties of MFC. To measure the degree of crystallinity, a typical method is X-ray diffraction (70-72). Obviously, the origin of the cellulose affects the degree of crystallinity and crystallite size. The degree of crystallinity can be around 70% of MFC obtained from wheat and straw soy (50), while a much lower value, 30%, was reported for the MFC obtained from beet pulp (73). Iwamoto et al. (59) reported the degree of crystallinity decrease with an increase in the number of passes because hornification of cellulose nanofiber under high shear forces, regardless of the origin of the cellulose. Moreover, the grinding process causes more damage to the crystalline structure of cellulose than homogenizer process and blender treatment (74, 75).

2.3.4 Specific surface area

MFC has a high specific surface area of about 50 m^2/g, compared with the specific surface area of the original fiber, which is about 5 m^2/g. The methods used for measuring specific surface area include BET measurement (which underestimates the real value), and Congo red absorption (76). It is also been reported that presence of lignin content decrease the value of specific surface area (76).

2.3.5 Suspension properties

The rheological property of MFC suspension is quite different from normal pulp suspension. It exhibits pseudoplastic and shear-thinning behavior (3,

26). Herrick (3) reported the viscosity of a 2% MFC suspension are 17400, 264, 136 MPa at 10, 1000, 5000 s^{-1}, respectively.

Pääkkö et al. (26) reported the MFC suspension displayed a gel-like behavior at a concentration of 0.125-5.9 wt%. He also observed that the storage modulus value of MFC is very high, 10000 Pa for a 3 wt% MFC suspension. Moreover, the storage modulus is almost 10 times higher than the loss moduli regardless of the suspension concentration. Another phenomenon about MFC suspension is that the viscosity decreases dramatically when the shear rate increases in a dynamic drainage jar (3). This is because a packing aggregation of MFC limits the formation of continuous network (77). Aulin et al. (78) reported the viscosity increases with the number of passes through the homogenizer device.

An interesting observation discovered by Fujisawa et al. (79) is that the pH affects the TEMPO-oxidation pretreated MFC suspension. As the pH of suspension decrease to about 2, the flowable dispersion becomes to a non-flowable gel, which is because the sodium carboxylate groups convert into free carbonyls. However, this phenomenon is reversible under certain condition, in which after washing, sanitation, and adjustment of the pH to 4.6, the suspension will be again transparent and flowable.

2.3.6 Film properties

MFC gel can be converted into film by two main methods: casting method, and vacuum filtration (21, 33, 44, 58, 59, 80, 81). A cellulose nanofiber network is formed through inter-fibril hydrogen bonding as the water is removed from MFC gel. Obviously, the properties of the films are highly depending upon two main factors: the film formation process and the MFC material used.

Many researchers have studied the mechanical properties of MFC films; however, a wide range of values was presented by different articles due to the difference of measurement methods, raw material and treatment processes. Zimmermann and Pöhler (47) reported the Young's modulus and tensile strength of MFC film are 6 GPa and 100 MPa, respectively.

While Berglund (82) reported the Young's modulus and strength of MFC film are 20 GPa and 240 MPa, respectively. Leitnera et al. (61) reported values of 9.4GPa and 104MPa for modulus of elasticity and tensile strength for sugar beet MFC film. Henriksson et al. (81) succeed in obtaining a strong MFC film with Young's modulus of 13.2 GPa and tensile strength of 214 MPa by a different approach. He introduced solvents other than water to modify the porosity of the film, in which the film consists of cellulose microfibril aggregates instead of individual microfibril. However, Syverud et al. (83) proposed that the maximum theoretical E-modulus can be 27 GPa, which is one-third of individual fibers.

In addition to the high strength properties, MFC film is usually transparent. That is because any particle with diameter less than one-tenth of visible light wavelength will not cause light scattering (84). Fukuzumi et al. (85) reported 78% and 90% light transmittance at 600 nm for 20 μm-thick TEMPO-oxidized MFC films with raw material of hardwood and softwood respectively. Siro (86) improved the light transmittance of MFC film at 600 nm for 20 μm thick films from 61% to 82% by subjecting MFC to three more passes through the homogenization. This is because the process disintegrates fiber aggregates. Moreover, by polishing the surface of MFC film with an optically transparent polymer layer, the light transmittance can be increased up to 90% (87).

2.4 Applications of microfibrillated cellulose

2.4.1 MFC composites

MFC as composite reinforcement has many advantages: remarkable mechanical properties, non-toxic, renewability, high flexibility for manufacturing process (44, 88). Nowadays, these advantages are being exploited in new high-value applications such as car construction composites, shipping crates and pallets, toys, storage bins, outdoor furniture and possible biomedical applications (88).

Due to its high Elastic modulus and high surface area, MFC allows for the formation of a highly dense hydrogen bonding network (89). MFC based

composite have been proved to have more inter fibril adhesion, higher fibril strength, and less defects compared with fiber-based composite (81, 89). Besides, MFC as a reinforcement material in polymer-based composites provides a huge improvement of the respective mechanical properties, such as bond density and toughness (44).

2.4.2 Packaging applications

Paper and board are widely used in modern packaging. MFC coated paper and MFC films as potential packaging materials have gained an increasing attention, especially for food packaging because of its great mechanical and barrier properties, as well as renewability and biodegradability.

Syverud et al. (83) reported the preparation of paper coated with MFC, in which MFC was deposited top side of a wet paper sheet by a dynamic sheet former. The result showed a decrease of air permeability as the basis weight of MFC layer increases. He observed that the air permeability decrease from 30000 nm $Pa^{-1}s^{-1}$ to 360 nm $Pa^{-1}s^{-1}$ as the basis weight for the MFC coated layer increase from 2 g/m^2 to 8 g/m^2. This is because the significant reduction of the surface porosity. Moreover Nygårds (90) reported that the use of carboxylated MFC formed denser coating layer that has superior air barrier property compared to enzymatically pretreated MFC. Besides the good air barrier property, another advantage of MFC coated packaging is higher oil-resistance, which is important for food packaging. Aulin et al. (78) pointed out that the oil resistance is improved as the air permeability of MFC coated packaging decreased. Hult et al. (91) used the combination of MFC and shellac to coat on the surface of paper as a multilayer structure with two coating layers. He reported the combination of multilayer system provides better air barrier property than those only coated with shellac, which is about 80%-90% improvement.

MFC films also have a good barrier property for water vapor, which is important for packaging. Normally, researchers use the water vapor transfer rate (WVTR), the volume of water vapor passing through a film

per unit area and time under certain conditions, to measure the barrier property against water vapour. Spence (76) and Venditt (92) studied the influence of different raw materials on WVTR of MFC films. The result shows the water barrier property of MFC films improved 20-30% compared with paper packaging. Moreover, the MFC film made from bleached hardwood showed a higher water barrier property than other fibers. They also reported that the lignin content in the MFC will decrease the value due to larger pores caused by low bonding potential. Minelli et al. (93) studied the influence of different pretreatments on WVTR of MFC films. The result shows that the pretreatment applied did not play a major role in water barrier property of MFC films.

All above mentioned studies show that MFC based material has a huge potential in packaging applications due to its remarkable mechanical properties, sufficient barrier to oxygen, water vapor, and oil. However, there are two main challenges that remain unresolved. The first one, which was mentioned earlier, is the energy consumption of MFC production. High energy consumption increases the price of MFC, which holds back the scale-up of applications. Another one is the difficulty of removing water from MFC slurry because of the huge specific surface area of MFC, which means it takes a great effort to remove the water and would likely create the need to modify standard paper machine processes.

2.4.3 Printing application

The use of MFC as a coating agent for printing applications, which can improve the print quality of synthetic paper has been presented recently. Hamada (94) coated the sheet with 3 wt% MFC suspension with a grammage of 3 g/m^2. The result shows that the rate of ink absorption decreased as the weight of MFC coating increased within the same contact time because the ink pigments may have been captured by the MFC layer near the surface, which is increasing the sheet resistance to ink penetration. Hamada also tried to change the coating formula by mixing clay and PVA with MFC. The result shows that the addition of MFC helped

to improve the flexographic print density and decreased the ink absorption rate (95).

2.5 Conclusion

Microfibrillated cellulose (MFC) as a nano sized biomaterial have been the focus of an increasing number of works and researches. Major studies over the last decades are shown that MFC could be used as fillers to improve mechanical and barrier properties of biocomposites. In addition, due to its properties, it has found various other uses and is particularly used in high-value applications, such as transparent films and porous dense aerogels. MFC can be extracted from various plant sources through mechanical separation. Homogenizer, microfluidizer and grinder are the most common devices for producing MFC. However, all the current methods require high energy input. Thus, new mechanical process, and new pre- and post- treatment are currently under development to reduce the high energy consumption and produce new types of MFC materials on an industrial scale.

The aim of this thesis is to produce useful fibrillated cellulose product by manipulating the sub-cell wall swelling of wood fibers and then refining in a conventional refiner. Two different pretreatment methods, as well as a customised Valley beater will be studied in the following work to achieve the goal.

3 Materials and methods

3.1 Pulp preparation

The raw material was bleached Kraft never dried birch pulp from Stora Enso Varkaus mill. Dry material content was approximately 9wt%.

All the pulp used in the following experiments was adjusted to sodium form. First, the pulp was diluted with deionized water to 2wt%. Then the pH of the pulp suspension was increased to 10 with NaOH and mixed for 15 minutes in room temperature. The excess alkaline was removed by filtration and the pulp was washed repeatedly with deionized water until the conductivity of the filtrate was less than 5 µS/cm.

The pulp was then pretreated with enzyme or “smart” polymer and refined with standard Valley beater or customized Valley beater for a certain time. The abbreviations and conditions for preparing different samples are summarized in Table 2. The details of chemicals and procedure used for pretreatment and the remodeling of the Valley beater will be discussed in following sections.

Table 2 The abbreviations and prepare conditions for all experiments.

Series	Refining time				
	0 min	7.5 min	15 min	30 min	60 min
Reference	REF 0	REF 7.5	REF 15	REF 30	REF 60
Cellulase pretreated	CEL 0	CEL 7.5	CEL 15	CEL 30	CEL 60
PAA pretreated	PAA 0	PAA 7.5	PAA 15	PAA 30	PAA 60
Customized Valley beater	CVB 0	CVB 7.5	CVB 15	CVB 30	CVB 60

3.1.1 Reference series

Pulp without any pretreatment was soaked in deionized water and then refined in a standard Valley beater. The total volume of suspension added into the Valley beater was 25l; however, the consistency of the suspension remained 1.57wt% as standard (ISO 5264/1-1979) required. After 5 minutes distinguish (without load), took out a 2l sample and then started refining with load. Took out 2.0L sample on 7.5, 15, 30, 60 minute and adjusted the samples to 10% DMC for following tests.

3.1.2 Cellulase pretreated series

ECOPULP® R from AB Enzymes was used in this experiment. It is a cellulase enzyme preparation produced using a genetically modified strain of Trichoderma reesei. The main activity is endo-1,4-β-D-glucanase. It is a clear, brown aqueous liquid with a density of approximately 1.0 - 1.1 g/ml.

First diluted the pulp to 1.5% DMC and adjusted the pH to 5. Then use the cooker to heat the pulp to 60°C. Added the enzyme (dosage: 2mg enzyme/gram pulp) to activate reaction. Mixed for 1 hour and kept the temperature stable around 60°C. After 1-hour reaction, raised the pH to 10 and mixed 15 minutes to kill the enzyme. The excess alkaline was removed by filtration and the pulp was washed repeatedly with deionized water until the conductivity of the filtrate was less than 5 µS/cm.

After pretreatment, refined the pulp same way as reference series.

3.1.3 PAA pretreated series

Polyacrylic acid (PAA) was used in this experiment. The molecular formula is $(C_3H_4O_2)_n$ and the molecular weight is about 5000, which the polymer is able to access into fibers at this size. Meanwhile PAA is an anionic polymer, which means many of the side chains of PAA will lose their protons and acquire a negative charge in a water solution at neutral pH. This gives PAA the ability to expand many times as their original volume, which would have effects on the inner structure of fibers.

First diluted the pulp to 1.5wt%. Added the PAA solution (dosage: 1% PAA/gram pulp) and adjusted the pH to 3.5. Mixed for 1 hour at room

temperature to enable the PAA to penetrate into the fibers evenly. Then raised the pH to 10 and mixed for 15 minutes to enable PAA expansion in fibers. The excess alkaline was removed by filtration and the pulp was washed repeatedly with deionized water until the conductivity of the filtrate was less than 5 μS/cm.

After pretreatment, refined the pulp same way as reference series.

3.1.4 Customized Valley beater series

As discussed before, the current mechanical treatments of producing MFC consume large amount of energy which is not suitable for commercial production. The initial idea of the modification of Valley beater is to improve the procedure and reduce the energy consumption.

This modification is focused on finding a more effective method to cut down fibers as microfibrillated cellulose is essentially a kind of nano-scale cellulose. Valley beater as the most popular laboratory refiner was modified in this experiment. The beater roll of the Valley beater is modified to sharp edges as Figure 6 showed. It is assumed that the sharp edges together with bedplate might effectively cutting down fibers. However, it is also predicted that the sharp edges might get dull rapidly during refining. All other parts remain as standard required.

The pulp samples are refined same way as reference series.

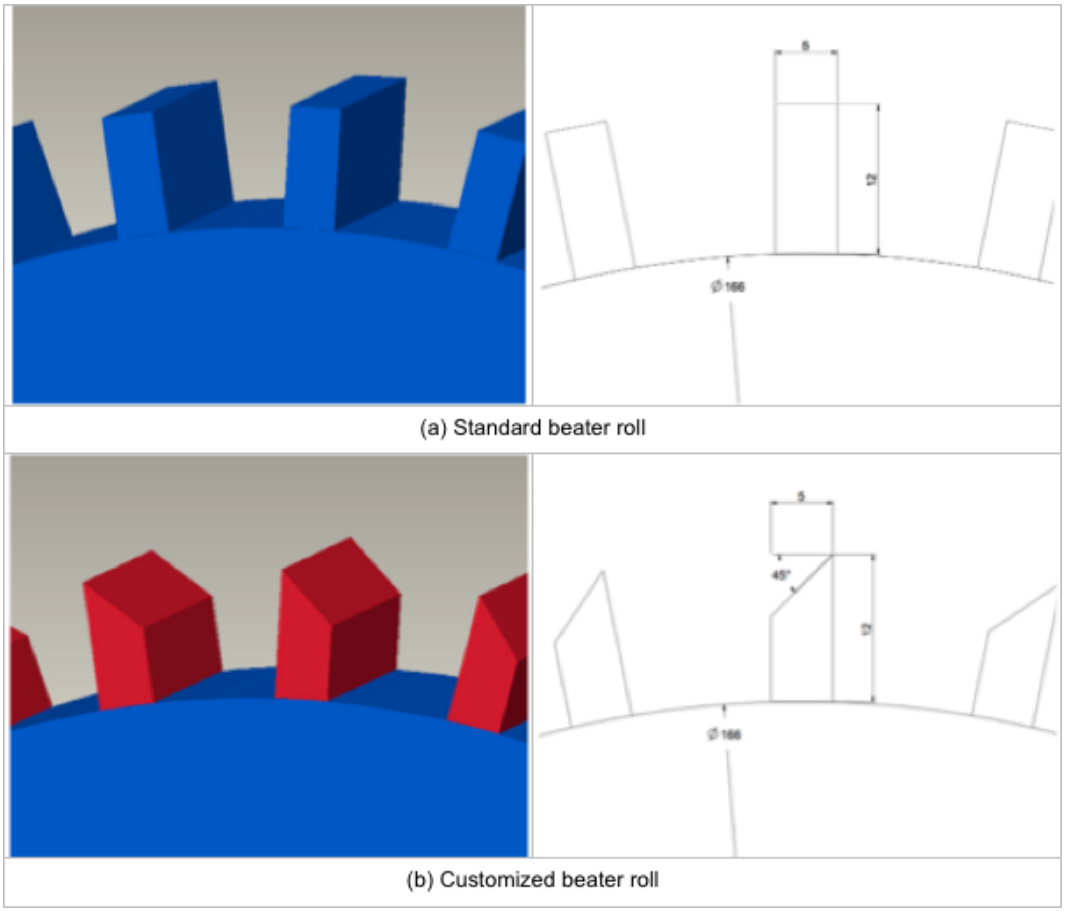

Figure 6 3D sketch and dimensions of beater roll before (a) and after modification (b).

3.2 Fiber analysis

3.2.1 Schopper Riegler Freeness

Schopper Riegler (°SR) is a traditional and most frequently used method for evaluating the refining result. The experiment is preceded according to standard (ISO5267-1).

3.2.2 Individual fiber

Fiber length and fiber cross-direction dimensions and distributions are important for determining the effectiveness of refining as well as improving the understanding of the relationships between fiber properties and paper properties. The FiberLab^{TM} fiber dimension analyzer (Figure 7) developed by Metso offers an easy and convenient way to measure fiber length, fiber width, fines content and Fibrillation percentage of samples.

This device analyses fiber flow through a narrow capillary at low consistency. Within the capillary a laser light source is used to control two CCD cameras which capture images of the fiber. These images are then processed by FiberLab software to provide several measurements, such as projected fiber length, fiber width, fiber wall thickness, average fines content, and fibrillation.

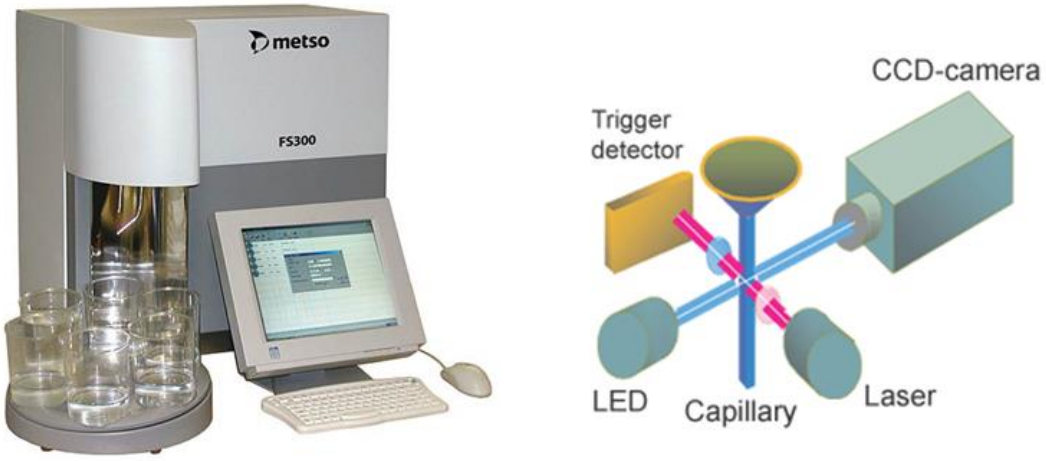

Figure 7 FiberLabTM fiber dimension analyzer and its test principle.

3.2.3 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is an excellent method to measure the nonfreezing water (NFW) and freezing bound water (FBW) in the fiber walls (96, 97). Water in the fiber wall which does not freeze is referred to as NFW. While water having a depressed melting temperature is referred to as FBW. The particular thermal behavior of the FBW is due to the increased pressure inside the pores in the cell wall. Bulk water (BW) is water which freeze at the same temperature as normal water. NFW and FBW accommodate in the micropores within the lingo-hemicellulose gel, while bulk water is held in the macropores between the microfibrills in the fiber cell wall.

DSC is a technique that measures the heat-flow rate against time or temperature when the temperature of the sample is changed according to

the premade temperature program. It is able to measure NFW, FBW and pore size distribution of pulp fibers with the isothermal melting method.

$$NFW = (W_W - \frac{\Delta H_t}{\Delta H_m}) * \frac{1}{W_S} \quad (1).$$

$$FBW = \frac{\Delta H}{\Delta H_m} * \frac{1}{W_S} \quad (2).$$

$$BW = FSP - (NFW + FBW) \quad (3).$$

ΔH_m is the specific heat of melting for normal water

ΔH_m is the absorbed heat for a complete melting transition for total freezing water (TFW)peak

ΔH_m is the melting heat for FBW peak

W_S is the mass of the dry solids

W_W is the mass of water in the sample

Moreover, researches by Manninen et al. (98) showed NFW is directly proportional to the hydrated surface area. They suggested that in water saturated polymer systems the amount of NFW may be used to measure the hydrated surface area with the following equation. The results have been proved fairly reasonably estimating the hydrated surface area, considering the water can penetrate the fibrils and access the outer surface of the elementary fibrils as well as amorphous regions of the cellulose.

$$Hydrated\ surface\ area = \frac{NFW}{0.35} * 1000 \quad (4).$$

3.2.4 Fiber saturation point

Fiber saturation point is a good method to measure the pore size distribution of pulp fibers by using dextran and sugars of different molecular weights. The solute exclusion test can be used to measure the amount of water inside the cell wall, the fiber saturation test. It is a good method to measure the degree of fiber swelling for pulp fibers, which is suitable for mechanical and chemical pulps and fines samples.

The basic principle of the test is that a solution of dextran polymer is added to a saturated sample of pulp. Two kinds of dextrans are used in this thesis, T6 and T2000 by Pharmacia. Dextran T6 is about 3.6nm which can be penetrated into fibers but not fibrils. Therefore only water inside of fibers but outside of fibrils dilutes the dextran solution. However, Dextran T2000 is about 54nm which is too large to enter into fiber wall. Therefore only water outside of the fibers dilutes the dextran solution. By knowing the concentration of dextran before and after addition to pulp, the weights of the dry fiber, water in the pulp and added dextran solution the FSP can be calculated.

$$FSP = \frac{W_{dex}+W_{water}}{W_{dried}} - \frac{W_{dex}}{W_{dried}} * \frac{\alpha_i}{\alpha_f} \quad (5).$$

W_{dex} *is the mass of dextran solution*

W_{water} *is the mass of water in the pulp*

W_{dried} *is the mass of bone dry pulp*

α_i *is the optical rotation of the dextran solution before addition to pulp*

α_f *is the optical rotation of the dextran solution after addition to pulp*

Moreover, with the degree of fiber swelling and fibril swelling, an estimated value of accessible surface area can be calculated with following equation.

$$Accessible\ surface\ area = (FSP_{T2000} - FSP_{T6})/0.01162355 \quad (6).$$

3.2.5 Water retention value

Water retention value (WRV) is a technique often used to measure fiber swelling, in which a pulp pad is centrifuged under conditions that are assumed to remove the water between the fibers. The moisture content of the pulp pad after centrifuging is a measure of fiber swelling. The value of WRV is depends on the specific test conditions (99, 100). In this thesis, the pad was centrifuged at a speed of 3000g for 15 minutes as specified by the standard SCAN-C 102 XE.

WRV test is simple, fast and precise to proceed. However, WRV is not suitable for heavily beaten or very poor draining chemical pulps. In order

to remain precision, a mix of 90% unbeaten bleached never dried birch pulp and 10% sample is measured. With the value of unbeaten bleached never dried birch pulp, it is possible to calculate the WRV value of each sample with following equation.

$$WRV = \frac{m_1 - m_2}{m_2} \quad (7).$$

m_1 is the mass of the centrifuged wet sample
m_2 is the mass of the oven-dry sample

Since the WRV value from above equation is an average value of 90% unbeaten bleached never dried birch pulp and 10% sample. The WRV of sample can be calculated by following equation (8).

$$WRV_{sample} = \frac{\mathrm{WRV} - 90\% * WRV_{unbeaten\ pulp}}{10\%} \quad (8).$$

3.2.6 Freeze drying

Outer surface area of fiber can be measured by adsorption using the BET isotherm with freeze drying technique. Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The freeze drying technique is similar to ordinary vacuum distillation, with one essential difference: the material to be dried must be solidly frozen below its eutectic point, before being subjected to a very low absolute pressure and a controlled heat input. Under these conditions the water content (in the form of an ice matrix) is selectively removed by sublimation. Then evaporate the nonfreezing water to cause the internal surface area to collapse. The outer surface area of fiber was obtained from a BET analysis of N2 adsorption isotherms (ASAP 2010, Micrometrics, USA).

3.2.7 Optical microscopy

Optical microscopy is a powerful and most frequently used technique to examine the fiber morphology. In this thesis, chosen wet samples are

examined by optical microscopy with magnifications of 10x and 20x respectively.

3.2.8 Scanning electron microscope

Scanning electron microscope (SEM) is another powerful and valuable technique to examine the fiber morphology. It provides more details and information than optical microscopy. In this thesis, chosen samples from BET surface area freeze drying are examined by SEM with magnifications of 100x, 200x, 500x and 1000x respectively.

3.3 Handsheet analysis

3.3.1 Handsheet forming

Due to the possible high drainage resistance of heavily refined sample, the handsheets made in this experiment is a mixture of 10% sample pulp and 90% sodium form unbeaten bleached birch pulp. Target basis weight of handsheet is set to 100 g/m^2 oven dry. C-PAM (dosage: 250g/ton o.d. pulp) is used as retention aid in this experiment to retain the small fiber particles.

The handsheets are made with a standard laboratory sheet former. The sheets are then couched from the wire with blotters, wet pressed, and dried in standard conditions (ISO 5269-1).

3.3.2 Handsheet testing

All the handsheets are conditioned in a standardized environment of 25℃ and 50% relative humidity (ISO 187). The sheets were cut with a punch of an area 141*141 mm. Testing were carried out according to standards: basis weight (ISO 536), thickness (ISO 534), bulk (ISO 534), ISO brightness (ISO 2470), opacity (ISO 2471), light scattering and absorption coefficient (ISO 9416), tensile strength (ISO 1924-2), air permeability (ISO5636).

4. Results and discussion

4.1 Characterization of pulps

4.1.1 Fiber length

During refining, individual fiber is shortened by the cutting effect of beater bars. Figure 8 demonstrates the average fiber length of cellulase pretreated series is much shorter than reference series and PAA pretreated series. The average fiber length of reference sample, cellulase pretreated sample, and PAA pretreated sample after 60 minutes refining are 0.48mm, 0.50mm and 0.3mm, respectively.

The disintegrating effect of cellulase enzyme treatment is obvious on cellulose fiber. During refining, the structure of individual fiber breaks and releases shorter fiber particles. This effect has a tremendous meaning for producing MFC with cellulase pretreatment since it can greatly decrease the energy consumption to achieve the same fiber length scale. Shorter fibers also affect the sheet strength property since less bonding area on single fiber. But it may produce an even sheet structure.

The average fiber length of customized Valley beater series is at the same level as reference series during the first 30 minutes refining, which indicate the cutting effect of customized Valley beater is the same as standard Valley beater. So the modification of the rotor does not affect the cutting effect of Valley beater. However, the average fiber length of customized Valley beater is shorter than reference at 60 minutes refining point. During the refining of different series, it is observed that the viscosity of pulp is higher than the one in standard Valley beater, which means more refining cycle during the same time period. This phenomenon happens mainly after 30 minutes refining and it might be one reason for shorter average fiber length of customized Valley beater sample than reference pulp sample under heavily beaten condition.

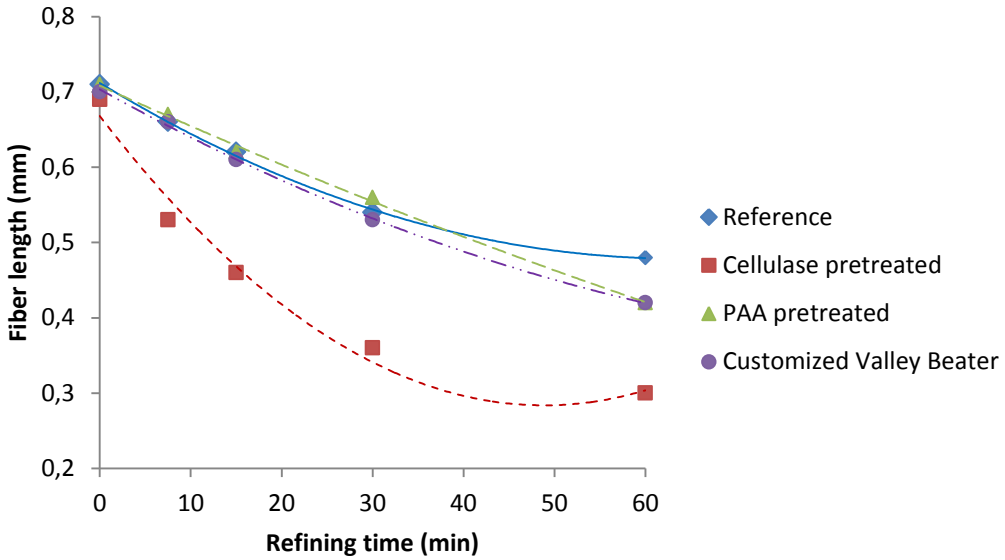

Figure 8 Fiber length of different series during refining measured by FiberLab™.

4.1.2 Fibrillation

As the refining continues, the fibrillation rate is increasing. Figure 9 shows the fibrillation of reference and pretreated series. The fibrillation of PAA pretreated series is higher than other two series after 15 minutes refining. A good fibrillation of the outer surfaces of the fibers is a prerequisite for strong bonding because the large surface area of fibrillation.

However, the fibrillation rate of customized Valley beater series is much lower than reference series. In addition, the increasing rate of fibrillation is also lower than the one refined by standard Valley beater. The fibrillation of customized Valley beater series is only 2.04%, while the fibrillation of reference series is 4.81%. This indicates the fibrillation effect of customized Valley beater is much smaller than the standard Valley beater. The fiber-fiber boding ability and fiber-water bonding ability will greatly decrease due to the lack of fibrillation, which affect the strength property and swelling property of pulp.

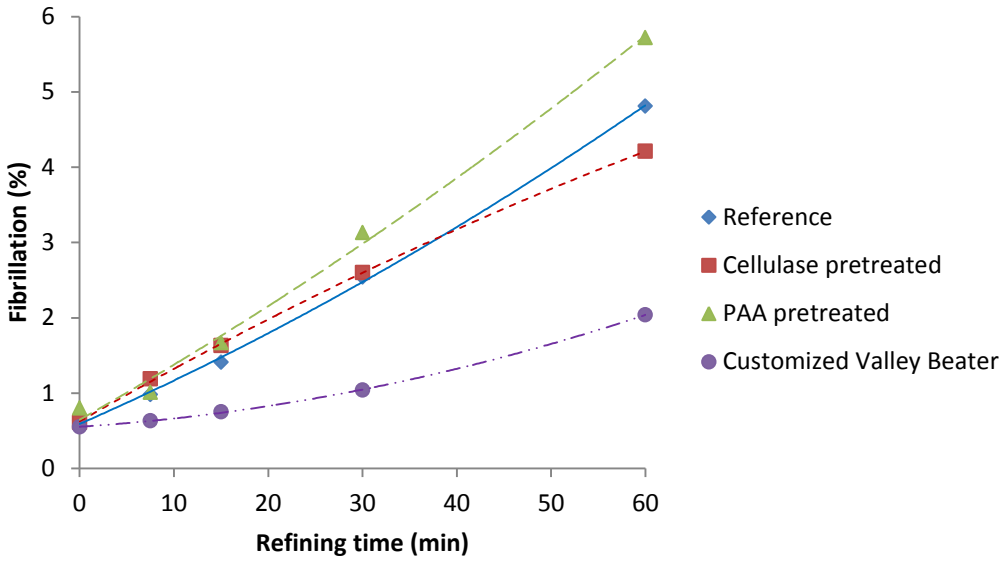

Figure 9 Fibrillation of different series during refining measured by FiberLab™.

4.1.3 Fines content

The fines content in pulp samples increase during refining. However, the increasing rates slow down after 30 minutes refining. Note that the fines content here is number average fines content measured with FiberLab™.

Figure 10 shows the number average fines content of PAA pretreated series and reference series are at the same level. However, the fines content of cellulase pretreated series is much higher than other two series. The fines amount of cellulase pretreated sample is about double than other two samples after 60 minutes refining. During cellulase pretreatment, the enzyme attack and disintegrate the fiber. As refining continues, the structure of individual fiber breaks and releases fines. Since specific surface area of fines (10-20 m^2/g) is several times that of fibers, fines can greatly increase interfiber bonding which is important for strength properties. Fines also affect the sheet density and surface properties.

The fines amount of customized Valley beater series is at the same level as reference series during the first 30 minutes refining and the number average fine content is a bit higher than the reference one. The reason may be due to the viscosity change rate of the pulp refined in two different

Valley beater discussed in fiber length result. However, due to poor fibrillation, the bonding capacity of fines here is significantly lower than that of fines formed with standard Valley beater, which means the fines quality is poorer compared with the one in reference series.

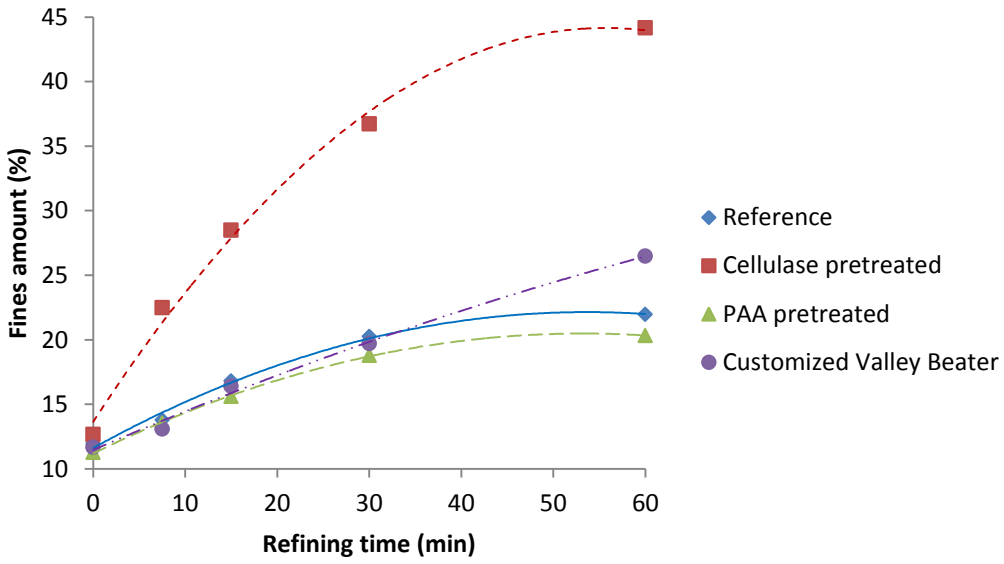

Figure 10 Number average fines content of different series during refining measured by FiberLab™.

4.1.4 Schopper Riegler

The Schopper Riegler (°SR) is widely used to track the changes in the drainage rate of various chemical pulps during refining, where the drainage rate is related to the surface conditions and swelling of the fibers. Therefore, the Schopper Riegler is highly corresponding to the physical properties of handsheets.

The °SR values rise as the refining time increase as showed in Figure 11. However, the °SR reaches the maximum value around 60 minutes because this method is no longer suitable to measure heavily refined pulps. Figure also shows the two pretreated series have great impact on the drainage rate of pulps. The two pretreated series gain higher °SR value then the reference series at the same refining time.

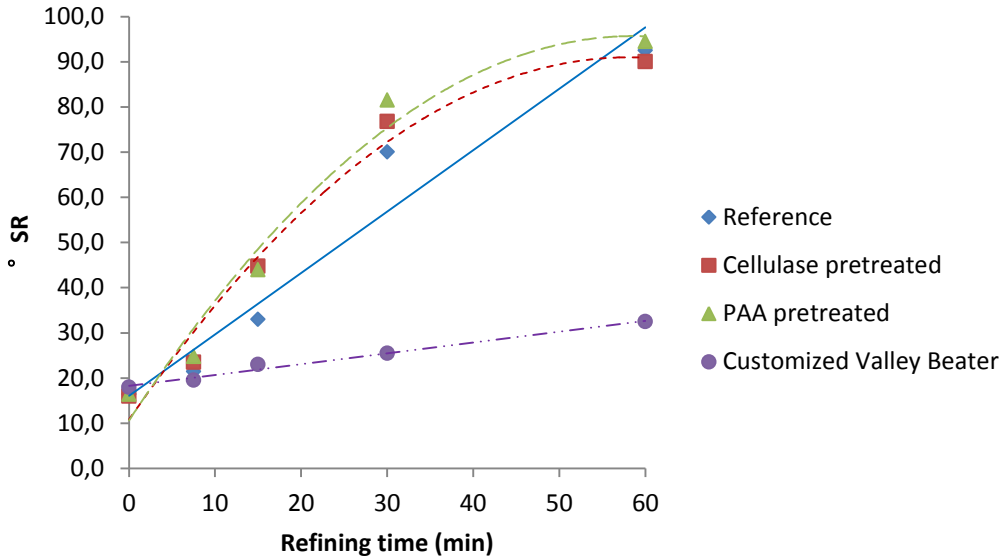

Figure 11 ° SR values of different series during refining.

However, °SR value of customized Valley beater series is way less than the standard valley beater series especially after 15 minutes. The °SR value of customized Valley beater sample is only 32.5, which is about the same value as 15 minutes refined in standard Valley beater. The high drainage resistance is caused by lacking of fibrillation.

4.1.5 Water retention value

Water retention value (WRV) is an empirical estimation of the fibers capacity for holding water. As stated in materials and methods chapter, WRV test is not suitable for heavily beaten pulp samples. So the WRV here are calculated values which give a reasonable approximation of fiber swelling.

Figure 12 shows the WRV increases with refining because of internal fibrillation. In addition, the fiber swelling ability of two pretreated series is better than reference series, which indicates two pretreated methods both disrupt the fiber structure and enhance the internal fibrillation.

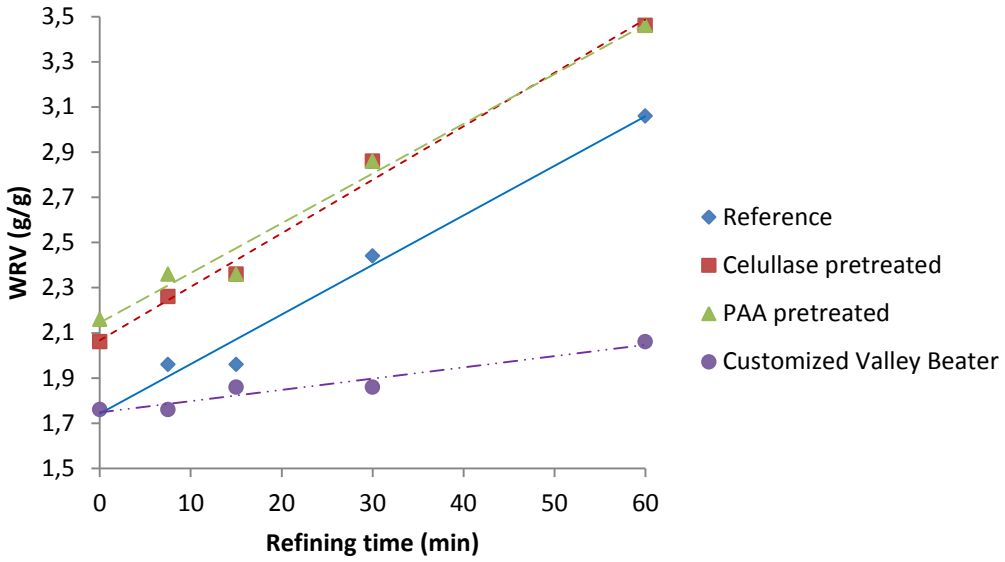

Figure 12 Water retention values of different series during refining.

As the Schopper Riegler results, WRV of customized Valley beater is way lower than reference series due to the lack of fibrillation. Once again, the results show the main effect of customized Valley beater on fibers is cutting but without fibrillation.

4.2 Fiber morphology

Fiber morphology is very helpful to gain a deep understanding on fiber properties, such as bonding ability, swelling ability and strength properties. Figure 13 shows the possible changes on fiber morphology during refining. The main effects of refining on fibers are as follows: removal of primary fiber wall, internal fibrillation and external fibrillation, fiber cutting, creation of fines, delamination, swelling and straightening of fibers.

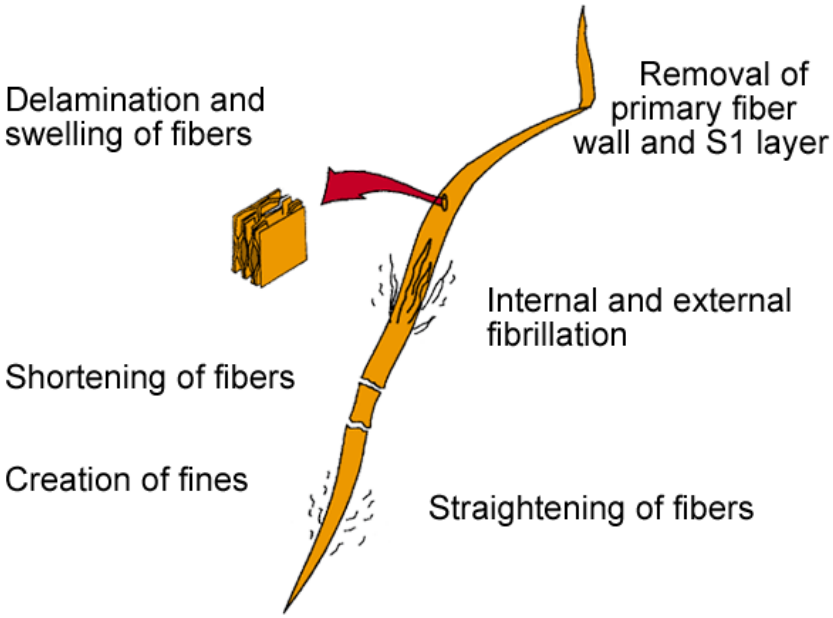

Figure 13 Main effects of refining on fibers (101).

4.2.1 Optical microscopy

Figure 14 shows the optical microscope images of different samples refined for 60 minutes. *Figure 14* (c) shows the cellulase pretreated sample have shorter fibers with more fines content. While *Figure 14* (b) shows the customized Valley beater sample have less fines and fibrillation compared with standard Valley beater samples.

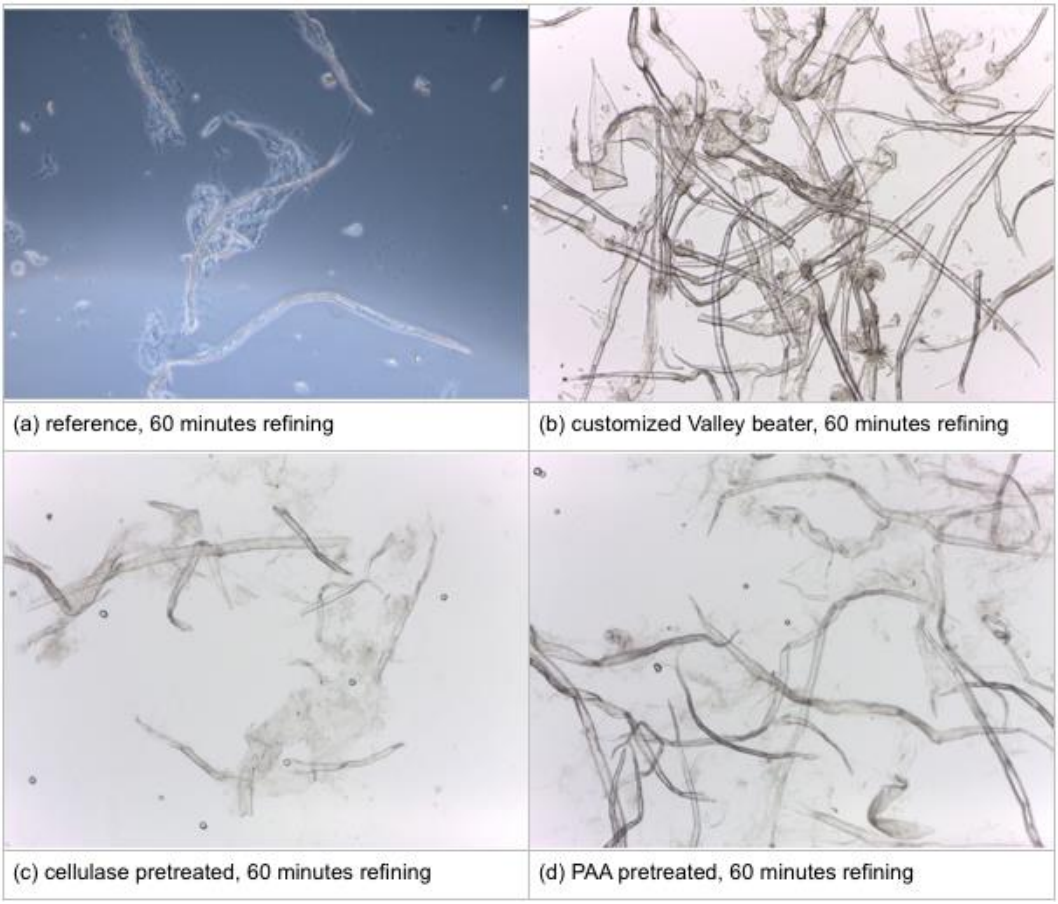

Figure 14 Optical microscope images of (a) reference sample, (b) customized Valley beater sample, (c) cellulase pretreated sample, (d) PAA pretreated sample refined for 60 minutes. Magnification of 10x.

4.2.2 Scanning electron microscope

Figure 15 shows the scanning electron microscope image of different samples refined for 60 minutes. Compared with other samples, sample refined by customized Valley beater still contains some unattacked fiber cell wall with much less external fibrillation. However, the cutted edge on fibers shows the main effect of customized Valley beater is shortening of fibers. Figure 15 (a), (b), (c) shows the original pulp fiber structure is partly destroyed and release nanofibers. However, the reference and PAA pretreated samples have a large aspect ratio of nanofibers than cellulase pretreated sample. It seems the cellulase randomly cleaves the cellulose fiber and results in small particles.

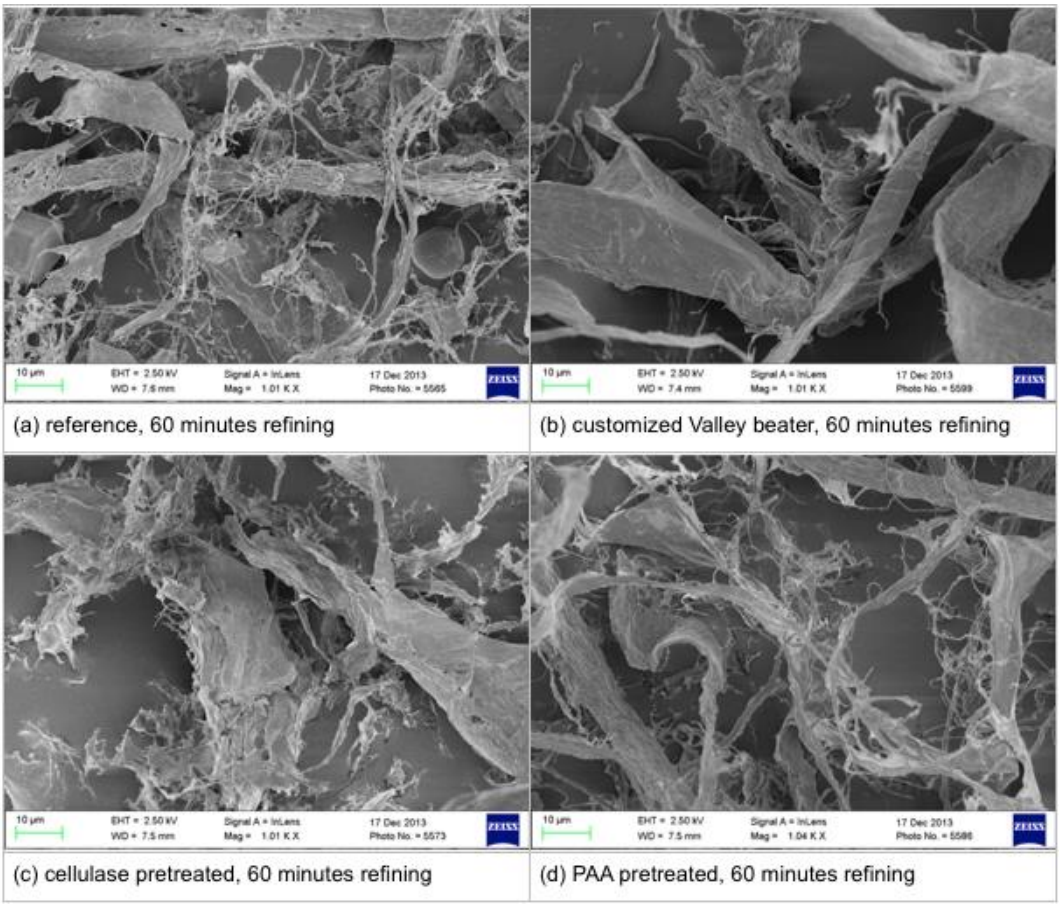

Figure 15 Scanning electron microscope images of (a) reference sample, (b) customized Valley beater sample, (c) cellulase pretreated sample, (d) PAA pretreated sample refined for 60 minute. Magnification of 1000x.

4.3 Fiber swelling properties and surface area

4.3.1 Swelling properties at different length scale

Swelling is relevant to many aspects of a material's behavior. For fibers, the degree of swelling is linked to dewatering, recyclability, strength development and fiber flexibility.

As discussed in the materials and methods chapter, two dextrans were used to measure the FSP, the degree of swelling. Dextran T6 is used to measure the fibril swelling and T2000 is used to measure the fiber swelling. The results are showed in Figure 16 and Figure 17.

Figure 16 demonstrates both pretreatments could largely improve the fibril swelling, especially the cellulase pretreatment. The fibril swelling degree of

unrefined cellulase pretreated sample is the same as 60 minutes refined nonpretreated sample. In addition, the fibril swelling degree of cellulase pretreated samples are very close to PAA pretreated samples expect the unrefined point, which indicates the different mechanism of two pretreatment methods. The cellulase cleaves internal bonds of cellulose and disrupts fibril aggregates. While PAA penetrated into fibers and mainly crush the fibril aggregates. As refining breaks down the cell wall and exposes the fibrils, the PAA pretreated samples show a great potential on fibril swelling.

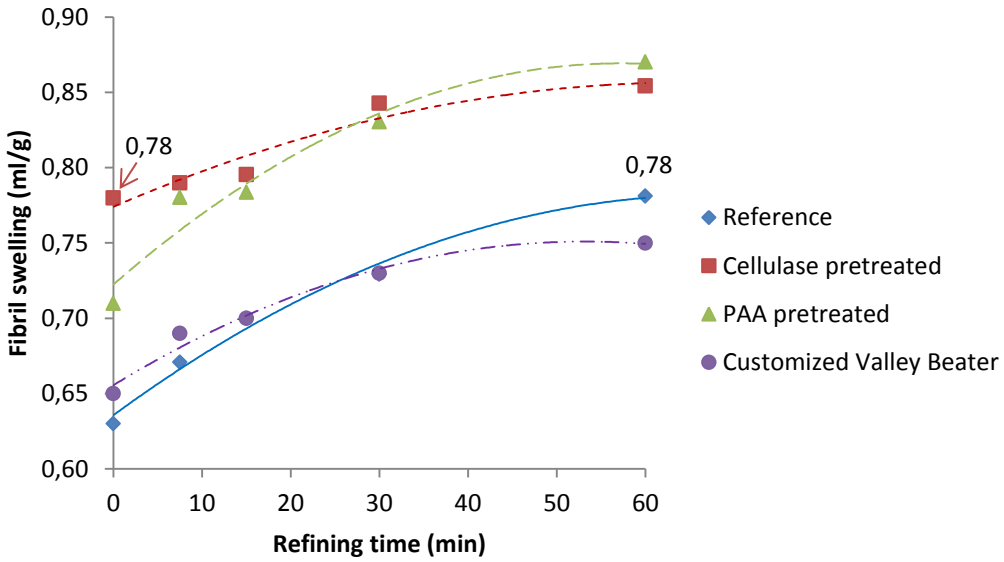

Figure 16 Fibril swelling degree of different series during refining measured with Dextran T6.

On the other hand, the fiber swelling remains the same for unrefined samples. This indicates it is possible to increase internal fibrillation of fibers without increasing the fiber swelling at all.

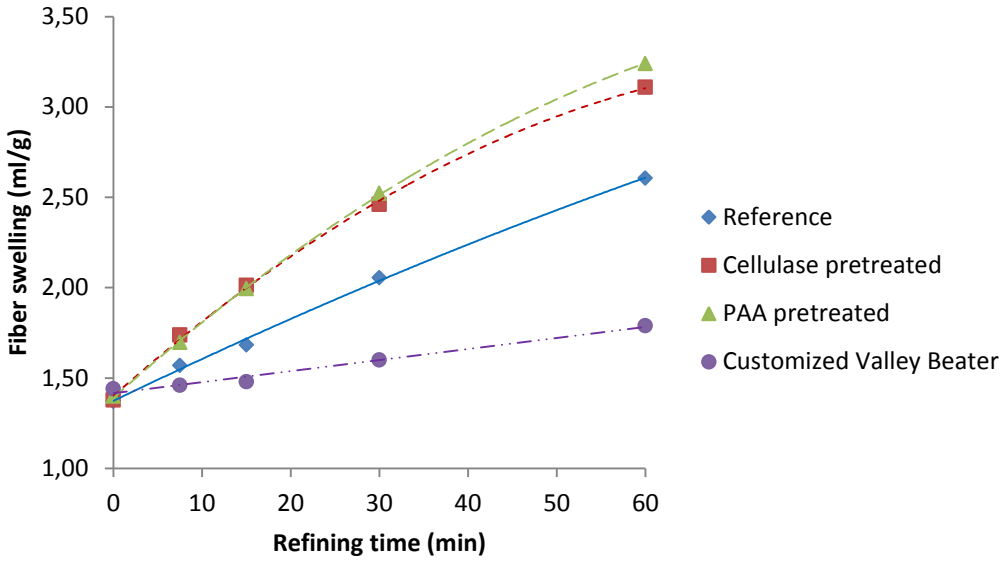

Figure 17 Fiber swelling degree of different series during refining measured with Dextran T2000.

4.3.2 Surface area at different length scale

Surface area is another key property of cellulose material. It is relevant to many other properties, such as fiber flexibility and strength properties. In addition, it is also extremely useful in gaining a deep understanding on material's behavior. With the newly developed methods at Aalto University, it is possible to give reasonable assumptions of surface area of cellulose materials at different length scales.

Outer surface area of fiber can be measured by adsorption using the BET isotherm with freeze drying technique. Accessible surface area can be calculated with the degree of fiber swelling and fibril swelling. Hydrated surface area can be calculated with the amount of nonfreezing water as these two values are directly proportional.

Figure 18 shows the results of surface area development during refining. Outer surface area of fiber cell wall is a critical property as the larger surface creates higher bonding ability. One promising application is to use it as reinforcement additive in paper production. The outer surface area increases during refining. However, the values of pretreated samples are

at the same level as reference, which suggests the pretreatment seems to have no impact on increasing the out surface area of fiber.

On the other hand, the accessible surface area values of pretreated samples are slightly higher than reference except for unrefined samples. The results indicate both PAA and cellulase mainly react inside of fiber cell wall and internally fibrillate fibers. In addition, the accessible surface area also increases during refining.

The hydrated surface area, however, remains at the same level during refining and the pretreatment also have little effect on the value.

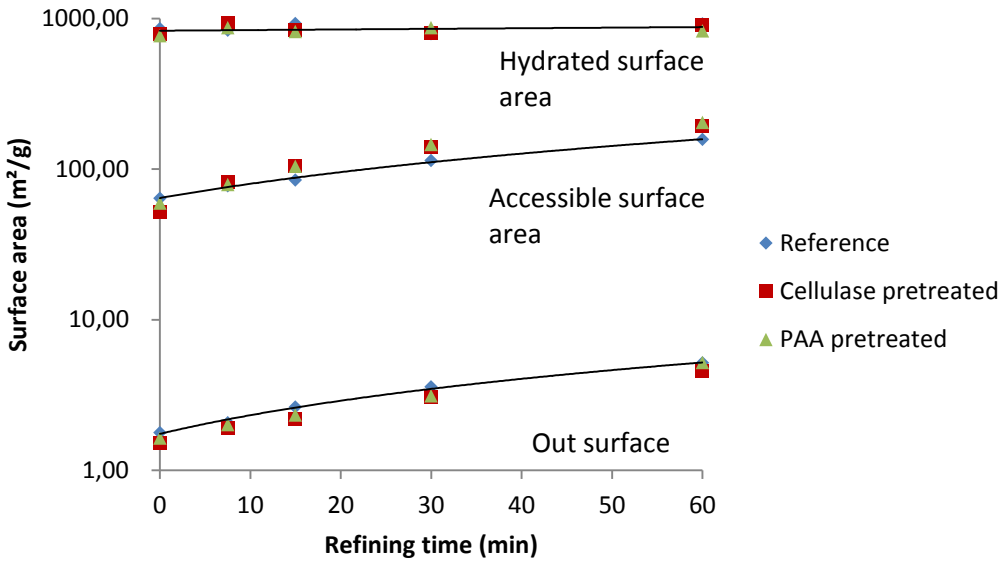

Figure 18 Surface area development at different length scales (Outer surface area, accessible surface area, and hydrated surface area).

4.4 Handsheet properties

Significant results were observed from the fiber properties and it is important to understand the effect of different pretreatment methods and modification of refiner on the pulp refining. Handsheets were made to gain a deep understanding of how the different pulp samples affect sheet properties

As mentioned in the method, the handsheet is made of mixture of 10% sample and 90% sodium form unbeaten birch pulp. However, the results of handsheet measurements suggest that the additive amount (10%) of sample is too low to observe clearly properties improvements. Another possible factor affecting the results is the using of C-PAM as retention aid.

4.4.1 Basic properties

Since the basis weight affects almost all the properties of sheet, the high stability of basis weight is required to analyse other properties of sheet. In this experiment, the target basis weight of handsheets is set to 110 g/m^2 o.d. and the real basis weight is 109.68±0.3 g/m^2 o.d. for 95% confidence level.

Bulk is another important basic property of sheet, which is the reverse of density. Refining creates fines and short fibers, which increase sheet density. Therefore as refining continuing, the bulk of sheets decrease in general (Figure 19).

The bulk of first two cellulase pretreated samples (0min, 7.5 min) are much lower than other sample. One reason may be because the pulp contains more primary fines after cellulase treatment. On the other hand, the main effect of customized Valley beater is cutting fibers without fibrillation; therefore, the amount of small fiber particles is way less than other series. So the bulk remains higher than other samples.

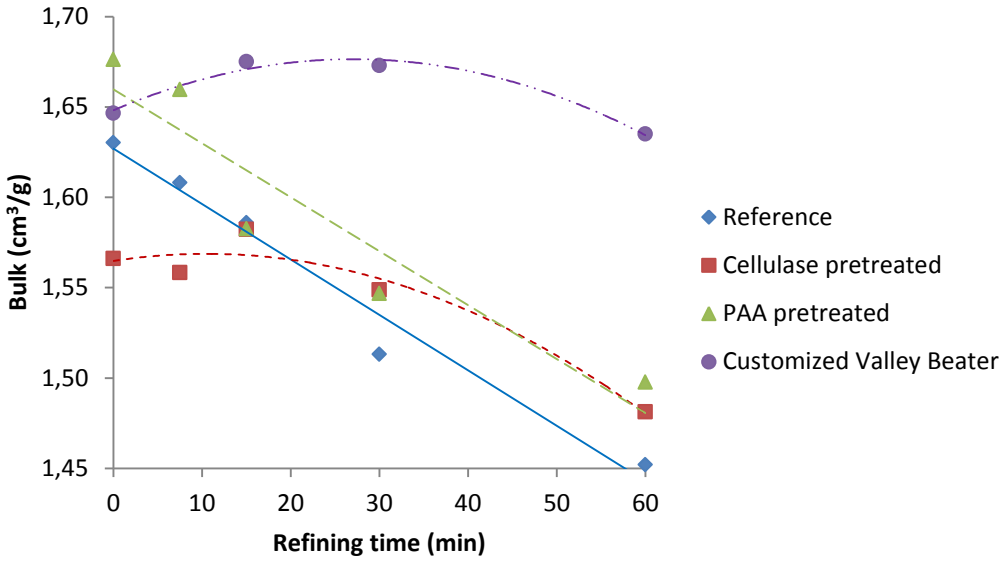

Figure 19 Bulk of handsheets (90% unbeaten pulp with 10% sample).

4.4.2 Optical properties

Figure 20 shows the brightness decrease as the refining continues. The 60 minutes refined point of cellulase pretreated sample is way lower than other samples. It is also observed that the original pulp is grey compared with other samples.

The reason for the brightness of chemical pulp deteriorates during refining is complicated. The refining causes the fibers to become more flexible and increase the outer surface area that enhance the bonding ability. In addition the fines amount in the pulp increases during refining. These effects cause changes in the pulp light scattering, and these changes reflect directly to the brightness of the pulp, on the basis of the Kubelka-Munk theory. The growth in the binding potential of the fibers and the diminishing effect of the bonds to the light scattering is greater than the optical effect of the fines forming in the refining.

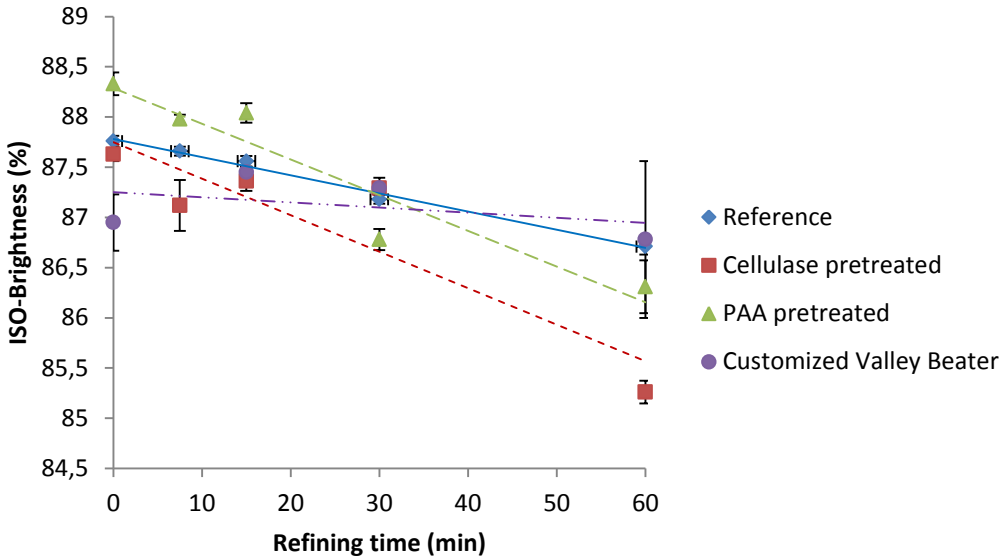

Figure 20 Brightness of handsheets (90% unbeaten pulp with 10% sample).

Refining affects the light scattering coefficient mostly in two different ways. Refining expands the free surface area of fibers, which increases the light scattering coefficient. On the other hand refining increases the amount of bonds between fibers and thus reduces the light scattering coefficient. The effect of the growing surface also diminishes because the partly loosened fibrils bind back to fiber. During drying the small particles created in refining, bind so intensely to fibers that the particles and fibers are in optical contact and do not increase the light scattering coefficient with their number. Therefor the light scattering coefficient value reach the maximum value around 10 minutes refining point according to Figure 21. The light scattering coefficients of pretreated series are bigger than the reference series, especially after 30 minutes refining. This indicates the pretreated pulps have more fibrillation and free surface area than reference pulp.

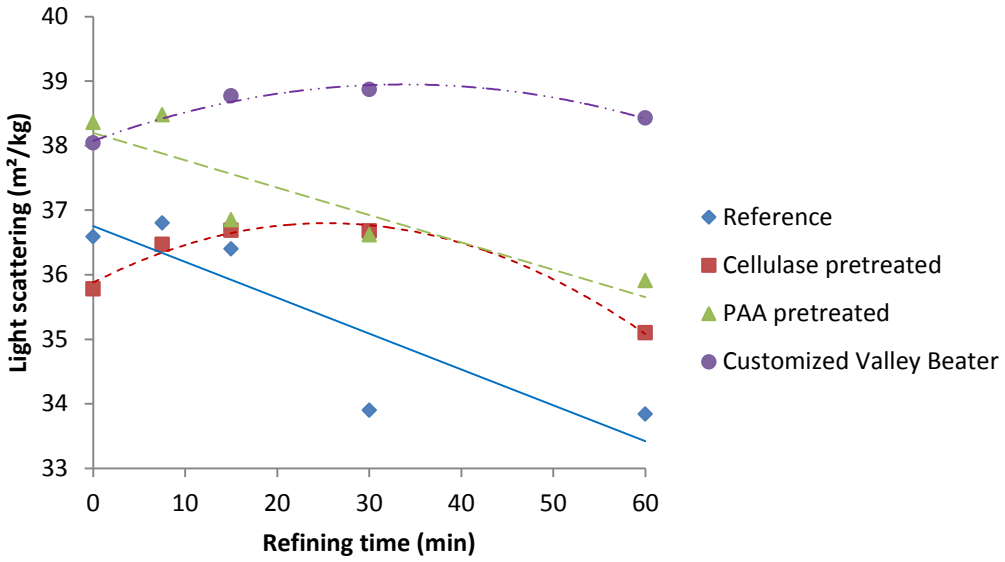

Figure 21 Light scattering of handsheets (90% unbeaten pulp with 10% sample).

4.4.3 Strength properties

In this experiment, tensile strength is measured to show the effect of different treatments on strength properties. Tensile strength is the highest loading rate a paper or board sample sheet can withstand without breaking, when being stretched in the surface direction.

Figure 22 and Figure 23 shows the tensile index and elastic modulus increase as the refining continues. Refining creates fibrillation and fines which largely increased the surface area and bonding ability. On the other hand, refining also shortens the fiber length, reduce the strength potential of fibers, thus leading to a compromise in individual fiber strength. Therefore, the strength properties of customized Valley beater series are way lower than other series due to the lack of fibrillation. However, Figure 22 shows the tensile strength of cellulase pretreated series is weaker than reference series. One possible reason is because the shorter average fiber length diminishes the individual fiber strength even though it contains more fines. On the other hand, the elastic modulus values of lightly refined points of cellulase pretreated samples are higher than other samples according to Figure 23.

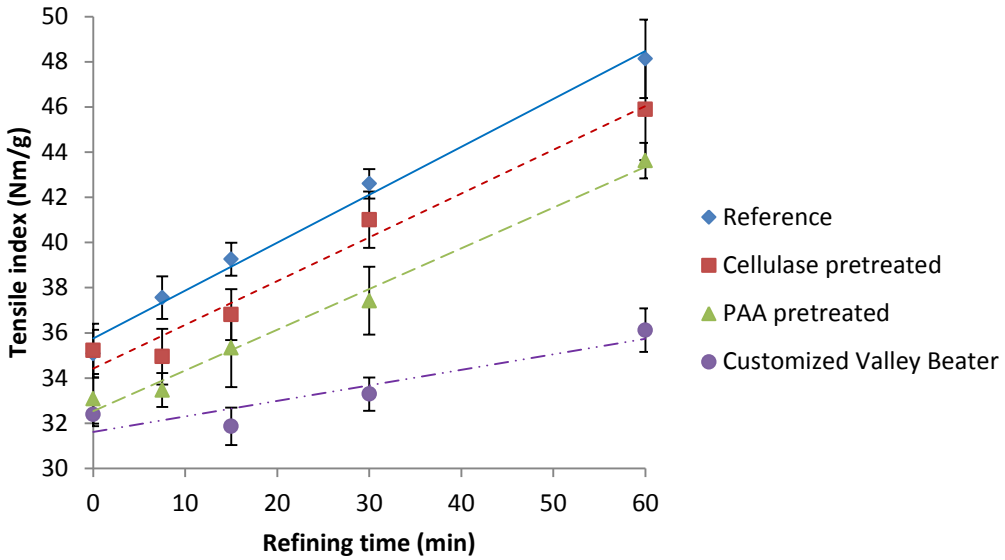

Figure 22 Tensile index of handsheets (90% unbeaten pulp with 10% sample).

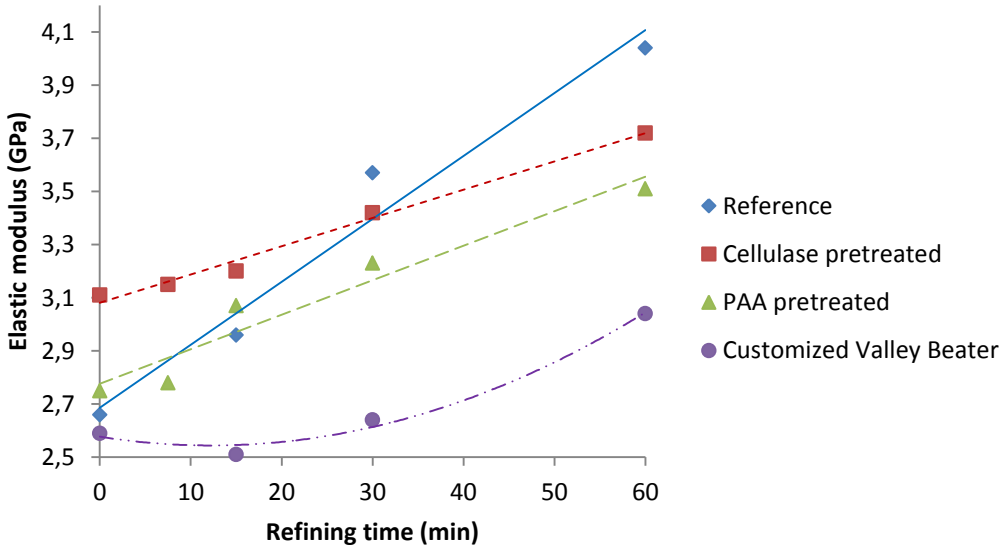

Figure 23 Elastic modulus of handsheets (90% unbeaten pulp with 10% sample).

5. Conclusions

The purpose of this thesis was to demonstrate the possibility of producing fibrillated cellulose product by manipulating the sub-cell wall swelling and then refining in a conventional Valley beater. In addition, a modified Valley beater was tested to study the effect of fiber cutting as a pretreatment.

Both pretreatment methods: cellulase hydrolysis and anionic polymer adsorption showed potential on manipulating the swelling property of cellulose fiber and facilitating disintegration of pulp during refining. The swelling results showed it is possible to increase internal fibrillation of fibers without increasing the fiber swelling by using both methods, especially by cellulase hydrolysis. In addition, the accessible surface area of pretreated samples is higher than reference pulp. However, the outer surface of pretreated samples remains the same as reference sample. Thus the strength properties of handsheets are not superior to reference. The cellulase hydrolysis samples consist of shorter fiber and more fines compared with reference. In addition, SEM images showed the cellulase randomly disrupt the cellulose fiber and left with small fiber particles. PAA pretreated samples were superior in fibrillation.

The results of customized Valley beater showed the sharp edge bars mainly shorten the fiber rather than fibrillate it compared with standard Valley beater. Therefore the swelling properties and strength properties of pulp were poor. However, the dewatering ability is superior to reference. It improved pulp flow especially under heavily beaten conditions and enabled more refining cycles compared with reference.

Under heavily beaten conditions, the pulp became gel-like material due to the high bonding ability of fiber and water. The velocity of pulp in the container reduce rapidly especially when refining over 60 minutes. Thus the Valley beater is no longer suitable for further refining the fiber. It is recommend to utilize two-stage refining (Valley beater, plus Masuko Ultra-fine friction grinder) combined with cellulase hydrolysis and anionic polymer absorption for further refining during future studies.

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Appendix

Appendix I Fiber results

Appendix II Handsheet results

Appendix III Optical microscopy and SEM image

Schopper Riegler results of all samples

Series	Beating time (min)	Temp. (℃)	Original SR	Pulp cake (g)	Adjustment (g)	SR value	AVG SR
Reference	0	22	17	2.1	-0.6	16.4	**16.4**
		22	17	2.1	-0.6	16.4	
	7.5	22	22.5	2.1	-0.8	21.7	**21.5**
		22	22	2.1	-0.8	21.2	
	15	22	33	2.1	0	33	**33.0**
		22	33	2.1	0	33	
	30	22	70	2.0	0	70	**70.0**
		22	70	2.0	0	70	
	60	22	92.5	2.0	0	92.5	**92.5**
		22	92.5	2.0	0	92.5	
Cellulase pretreated	0	22	16	2.0	0	16	**16.0**
		22	16	2.0	0	16	
	7.5	22	23	2.0	0	23	**23.5**
		22	24	2.0	0	24	
	15	22	44.5	2.0	0	44.5	**44.8**
		22	45	2.0	0	45	
	30	22	76.5	2.0	0	76.5	**76.8**
		22	77	2.0	0	77	
	60	22	90	2.0	0	90	**90.0**
		22	90	2.0	0	90	
PAA pretreated	0	22	17	2.1	-0.6	16.4	**16.4**
		22	17	2.1	-0.6	16.4	
	7.5	22	24.5	2.0	0	24.5	**24.8**
		22	25	2.0	0	25	
	15	22	44	2.0	0	44	**44.0**
		22	44	2.0	0	44	
	30	22	81	2.0	0	81	**81.5**
		22	82	2.0	0	82	
	60	22	95	2.0	0	95	**94.5**
		22	94	2.0	0	94	
Customized Valley Beater	0	18	18	2.0	0	18	**18.0**
		18	18	2.0	0	18	
	7.5	18	20	2.0	0	20	**19.5**
		18	19	2.0	0	19	
	15	18	23	2.0	0	23	**23.0**
		18	23	2.0	0	23	
	30	18	25	2.0	0	25	**25.5**
		18	26	2.0	0	26	
	60	18	32.5	2.0	0	32.5	**32.5**
		18	32.5	2.0	0	32.5	

Individual fiber properties of all samples measured with FiberLab™

Series	Beating time (min)	Fiber legth (mm)	Fines amount (%) number average	Fines amount (%) Length weighted	Fiber Width (um)	Fibrillation (%)
Reference	0	0.71	11.95	1.74	19.8	0.64
	7.5	0.66	13.79	2.21	20	0.98
	15	0.62	16.81	2.92	20.1	1.41
	30	0.54	20.26	4.26	20.5	2.54
	60	0.48	21.96	5.36	21.6	4.81
Cellulase pretreated	0	0.69	12.66	1.9	19.8	0.61
	7.5	0.53	22.49	4.5	19.9	1.19
	15	0.46	28.48	6.78	19.8	1.63
	30	0.36	36.72	11.28	19.7	2.6
	60	0.3	44.15	16.92	19.5	4.21
PAA pretreated	0	0.71	11.27	1.68	19.7	0.8
	7.5	0.67	13.54	2.13	20.2	1.01
	15	0.62	15.63	2.69	20.5	1.67
	30	0.56	18.8	3.68	21.4	3.13
	60	0.42	20.32	4.67	22.7	5.72
Customized Valley Beater	0	0.7	11.68	1.75	19.7	0.55
	7.5	0.66	13.09	2.17	19.5	0.63
	15	0.61	16.42	3.01	19.5	0.75
	30	0.53	19.71	4.16	19.5	1.04
	60	0.42	26.47	7.13	18.9	2.04

Water retention values of all samples

Series	Beating time (min)	WRV (g/g)	StDev	Confidence
Reference	0	1.76	0.01	0.0098
	7.5	1.96	0.0053	0.0052
	15	1.96	0.0088	0.0087
	30	2.44	0.004	0.0039
	60	3.06	0.0052	0.0051
Celullase pretreated	0	2.06	0.0042	0.0041
	7.5	2.26	0.0049	0.0048
	15	2.36	0.0016	0.0015
	30	2.86	0.003	0.0029
	60	3.46	0.0071	0.0069
PAA pretreated	0	2.16	0.0051	0.005
	7.5	2.36	0.0071	0.0069
	15	2.36	0.0132	0.013
	30	2.86	0.0086	0.0084
	60	3.46	0.0045	0.0044
Customized Valley Beater	0	1.76	0.0031	0.0031
	7.5	1.76	0.0089	0.0087
	15	1.86	0.0056	0.0055
	30	1.86	0.0044	0.0044
	60	2.06	0.0029	0.0029

Swelling properties and surface area of all samples

Series	Beating time (min)	FSP (g/g)		Accessible surface area (m^2/g)	Outer surface area (m^2/g)	FBW (g/g)	NFW (g/g)	Hydrated surface area (m2/g)
		T6	T2000					
Reference	0	0.63	1.37	64	1.78	0.44	0.30	857
	7.5	0.67	1.57	77	2.07	0.42	0.29	833
	15	0.70	1.68	85	2.63	0.50	0.32	925
	30	0.73	2.05	114	3.58	0.56	0.28	791
	60	0.78	2.61	157	5.16	0.71	0.32	919
Cellulase pretreated	0	0.78	1.38	51	1.50	0.47	0.27	784
	7.5	0.79	1.74	82	1.91	0.44	0.32	928
	15	0.80	2.01	105	2.20	0.46	0.29	830
	30	0.84	2.46	139	3.04	0.56	0.28	796
	60	0.85	3.11	194	4.54	0.85	0.31	896
PAA pretreated	0	0.71	1.40	59	1.64	0.40	0.27	767
	7.5	0.78	1.70	79	2.01	0.42	0.30	869
	15	0.78	1.99	104	2.32	0.47	0.29	817
	30	0.83	2.52	146	3.12	0.51	0.30	868
	60	0.87	3.24	204	5.20	0.68	0.29	825
Customized Valley Beater	0	0.65	1.44	68	1.63	0.43	0.20	571
	7.5	0.69	1.46	66	1.80	0.45	0.25	714
	15	0.70	1.48	67	1.88	0.45	0.23	657
	30	0.73	1.60	75	2.54	0.47	0.22	629
	60	0.75	1.79	89	3.04	0.49	0.26	743

Basic properties of handsheets (90% unbeaten pulp and 10% samples)

Series	Beating time (min)	Basis weight,g/m2	Thickness, um	Bulk, cm²/g	Density, g/cm²
Reference	0	109.98	179.3	1.63	0.61
	7.5	110.44	177.6	1.61	0.62
	15	110.22	174.8	1.59	0.63
	30	109.64	165.9	1.51	0.66
	60	111.08	161.3	1.45	0.69
Cellulase pretreated	0	109.57	171.6	1.57	0.64
	7.5	109.51	170.65	1.56	0.64
	15	108.77	172.1	1.58	0.63
	30	109.02	168.85	1.55	0.65
	60	109.03	161.5	1.48	0.68
PAA pretreated	0	108.93	182.6	1.68	0.60
	7.5	108.76	180.5	1.66	0.60
	15	109.53	173.35	1.58	0.63
	30	110.23	170.5	1.55	0.65
	60	109.5	164	1.50	0.67
Customized Valley Beater	0	110.29	181.6	1.65	0.61
	15	110.8	185.6	1.68	0.60
	30	109.45	183.1	1.67	0.60
	60	109.85	179.6	1.63	0.61

Optical properties and surface properties of handsheets (90% unbeaten pulp and 10% samples)

Series	Beating time (min)	Air permeability, ml/min	StDev	ISO-Brightness	StDev	Confidence	Opacity	StDev	Confidence	Light scattering m2/kg	light absorption m2/kg
Reference	0	2570	60.1	87.76	0.06	0.05	85.87	0.07	0.06	36.59	0.12
	7.5	2325	91.5	87.66	0.05	0.04	85.91	0.09	0.08	36.8	0.11
	15	2122	53.8	87.56	0.06	0.05	85.67	0.16	0.14	36.4	0.12
	30	1463	58.1	87.18	0.05	0.04	84.96	0.12	0.11	33.9	0.11
	60	900	31.4	86.71	0.09	0.08	85.07	0.03	0.03	33.84	0.12
Cellulase pretreated	0	2231	22.1	87.63	0.08	0.07	85.6	0.06	0.05	35.78	0.12
	7.5	2005	133.4	87.12	0.29	0.25	86.18	0.3	0.26	36.47	0.12
	15	2119	73.7	87.36	0.11	0.10	85.83	0.24	0.21	36.69	0.11
	30	1551	71.7	87.29	0.06	0.05	85.64	0.23	0.20	36.68	0.12
	60	978	78.7	85.26	0.13	0.11	86.19	0.11	0.10	35.1	0.17
PAA pretreated	0	2966	73.4	88.33	0.13	0.11	86.48	0.12	0.11	38.36	0.11
	7.5	2676	116.7	87.98	0.05	0.04	86.41	0.06	0.05	38.48	0.11
	15	2139	69.8	88.04	0.11	0.10	85.88	0.15	0.13	36.85	0.11
	30	1614	66.5	86.78	0.12	0.11	86.13	0.06	0.05	36.62	0.13
	60	1153	31.2	86.31	0.3	0.26	85.88	0.22	0.19	35.91	0.14
Customized Valley Beater	0	2920	73.6	86.95	0.32	0.28	86.94	0.14	0.12	38.04	0.13
	7.5	2634	108.1	87.34	0.05	0.04	85.94	0.05	0.04	37.01	0.12
	15	2979	71.2	87.45	0.06	0.05	86.91	0.11	0.10	38.77	0.12
	30	2960	99.2	87.29	0.12	0.11	86.87	0.12	0.11	38.87	0.12
	60	2573	64.4	86.78	0.89	0.78	86.99	0.35	0.31	38.43	0.13

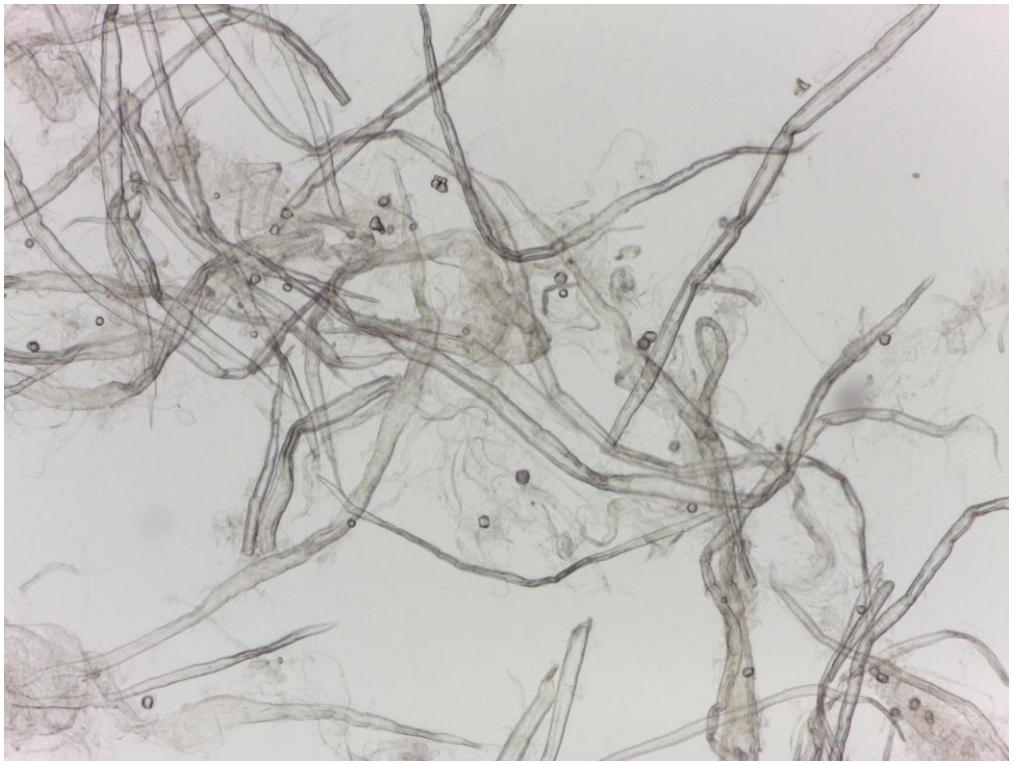
Strength properties of handsheet (90% unbeaten pulp and 10% samples)

Series	Beating time (min)	Tensile strength, kN/m	StDev	Confidence	Tensile index	StDev	Confidence	Elastic modulus	Tensile Stiff. kN/m	StDev	Confidence
Reference	0	3.86	0.187	0.116	35.08	1.70	1.05	2.66	477.05	167.78	103.99
	7.5	4.15	0.169	0.105	37.56	1.53	0.95	3.27	580.74	13.68	8.48
	15	4.33	0.129	0.080	39.26	1.17	0.73	2.96	517.12	193.99	120.23
	30	4.67	0.115	0.071	42.6	1.05	0.65	3.57	592.17	41.77	25.89
	60	5.35	0.312	0.193	48.13	2.81	1.74	4.04	652.46	19.90	12.33
Cellulase pretreated	0	3.86	0.21	0.130	35.22	1.92	1.19	3.11	533.07	23.81	14.75
	7.5	3.83	0.218	0.135	34.95	1.99	1.23	3.15	536.73	16.89	10.47
	15	4	0.198	0.123	36.81	1.82	1.13	3.2	550.94	33.43	20.72
	30	4.47	0.219	0.136	41.01	2.01	1.25	3.42	577.19	33.43	20.72
	60	5	0.396	0.245	45.89	3.63	2.25	3.72	601.25	38.37	23.78
PAA pretreated	0	3.6	0.193	0.120	33.08	1.77	1.10	2.75	501.52	34.87	21.61
	7.5	3.64	0.132	0.082	33.47	1.21	0.75	2.78	501.14	19.05	11.81
	15	3.9	0.308	0.191	35.34	2.81	1.74	3.07	527.49	22.91	14.20
	30	4.12	0.267	0.165	37.42	2.42	1.50	3.23	550.51	54.33	33.68
	60	4.78	0.139	0.086	43.63	1.27	0.79	3.51	574.83	20.08	12.44
Customized Valley Beater	0	3.57	0.092	0.057	32.39	0.83	0.52	2.59	470.12	33.56	20.80
	7.5	3.89	0.161	0.100	35.7	1.48	0.92	2.83	510.25	14.98	9.28
	15	3.53	0.148	0.092	31.87	1.34	0.83	2.51	466.09	32.41	20.09
	30	3.64	0.131	0.081	33.29	1.20	0.74	2.64	482.66	58.88	36.49
	60	3.97	0.17	0.105	36.12	1.55	0.96	3.04	545.4	17.78	11.02

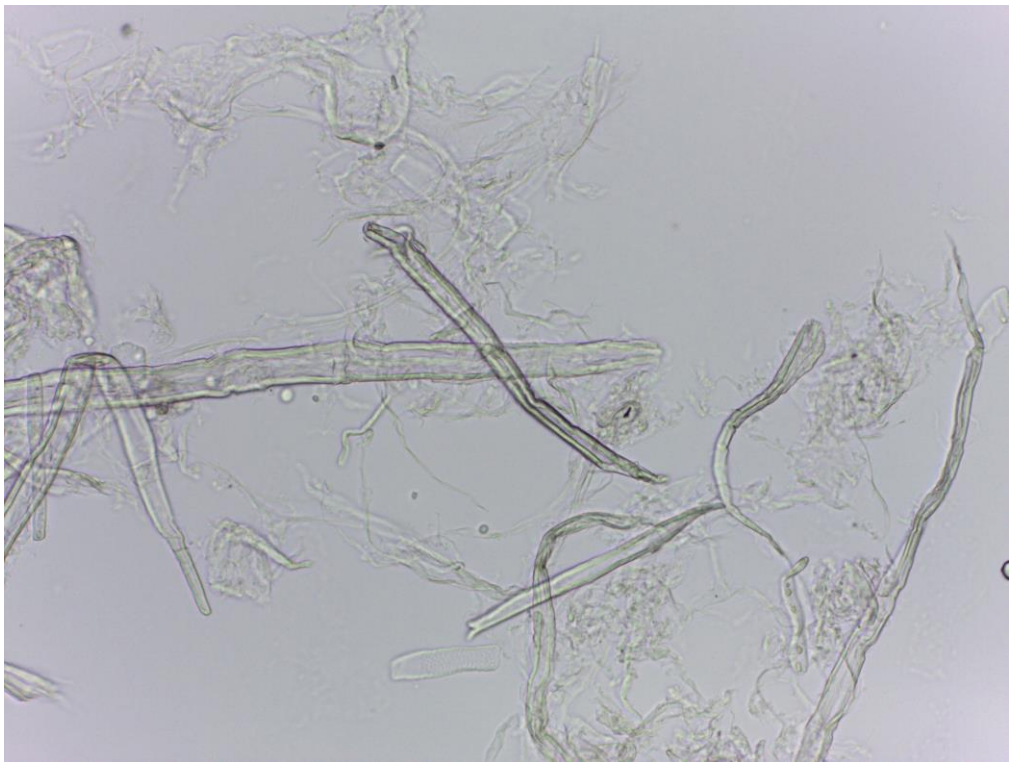
Strength properties of handsheet (90% unbeaten pulp and 10% samples).

Series	Beating time (min)	Elongation, %	StDev	Confidence	Breaking Length km	TEA J/m²	StDev	Confidence	TEA Index J/g
Reference	0	3.53	1.287	0.80	3.58	115.46	14.03	8.69	1.05
	7.5	3.92	0.275	0.17	3.83	124.48	12.76	7.91	1.13
	15	3.66	1.397	0.87	4	135.7	10.45	6.48	1.23
	30	4.2	0.345	0.21	4.34	148.4	12.02	7.45	1.35
	60	4.87	0.485	0.30	4.91	195.08	27.29	16.91	1.76
Cellulase pretreated	0	4.05	0.386	0.24	3.59	117.85	15.00	9.30	1.08
	7.5	3.86	0.328	0.20	3.56	111.73	14.13	8.76	1.02
	15	3.84	0.367	0.23	3.75	116.57	14.91	9.24	1.07
	30	4.22	0.342	0.21	4.18	141.8	15.98	9.91	1.30
	60	4.49	0.528	0.33	4.68	166.16	26.80	16.61	1.52
PAA pretreated	0	3.72	0.345	0.21	3.37	101.25	12.23	7.58	0.93
	7.5	3.87	0.257	0.16	3.41	106.72	9.51	5.89	0.98
	15	4.01	0.573	0.36	3.6	118.8	25.51	15.81	1.08
	30	4.15	0.915	0.57	3.81	127.97	31.60	19.59	1.16
	60	4.72	0.487	0.30	4.45	165.14	20.73	12.85	1.51
Customized Valley Beater	0	3.84	0.248	0.15	3.3	102.74	7.90	4.90	0.93
	7.5	3.84	0.248	0.15	3.61	122.48	14.48	8.98	1.12
	15	3.56	0.305	0.19	3.25	94.47	11.98	7.43	0.85
	30	3.53	0.231	0.14	3.39	96.53	8.51	5.28	0.88
	60	3.78	0.304	0.19	3.68	113.51	12.10	7.50	1.03

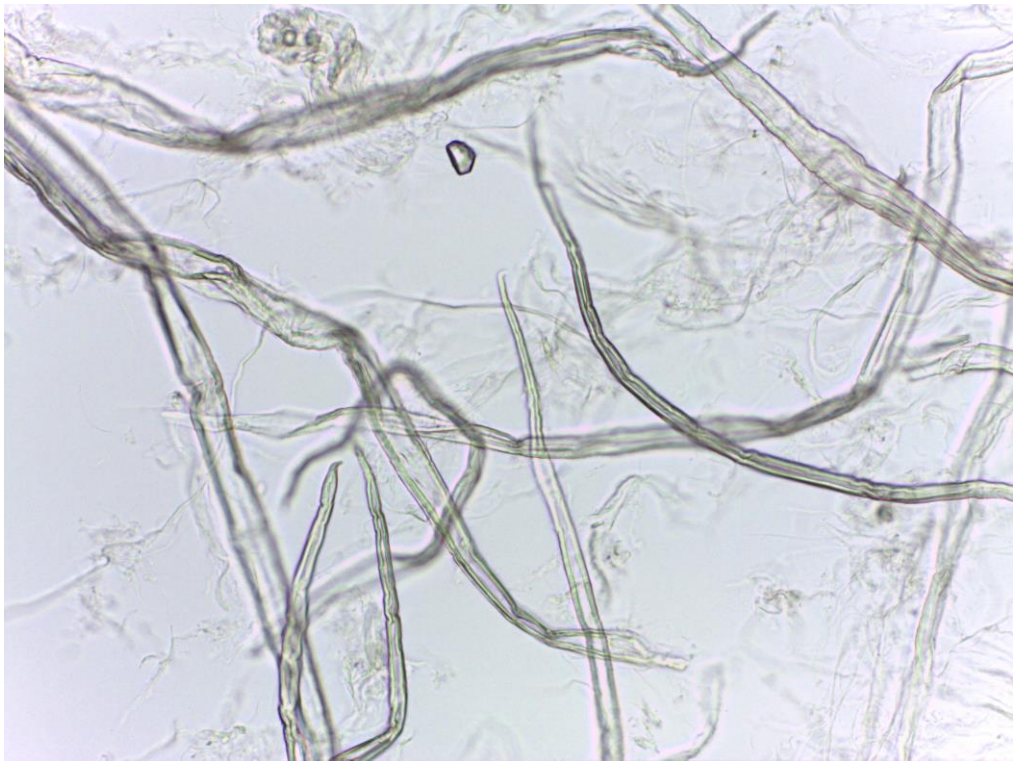
Optical microscope image of reference, 60 minutes refined sample. Magnification of 20x.



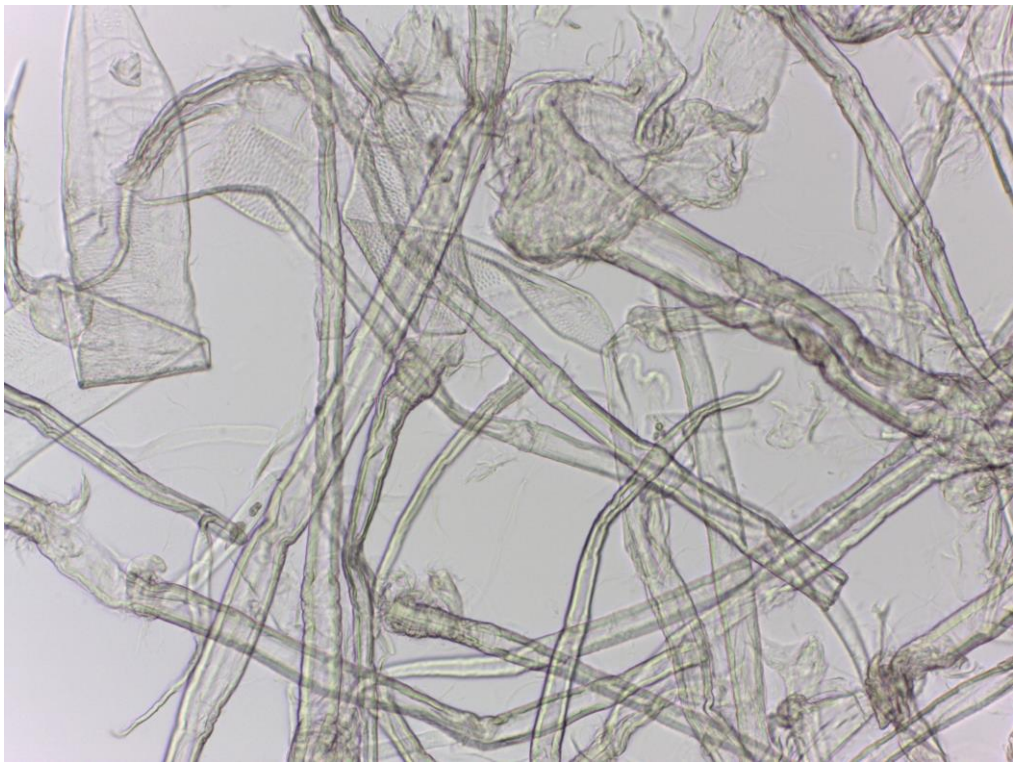
Optical microscope image of cellulase treated, 60 minutes refined sample. Magnification of 20x.



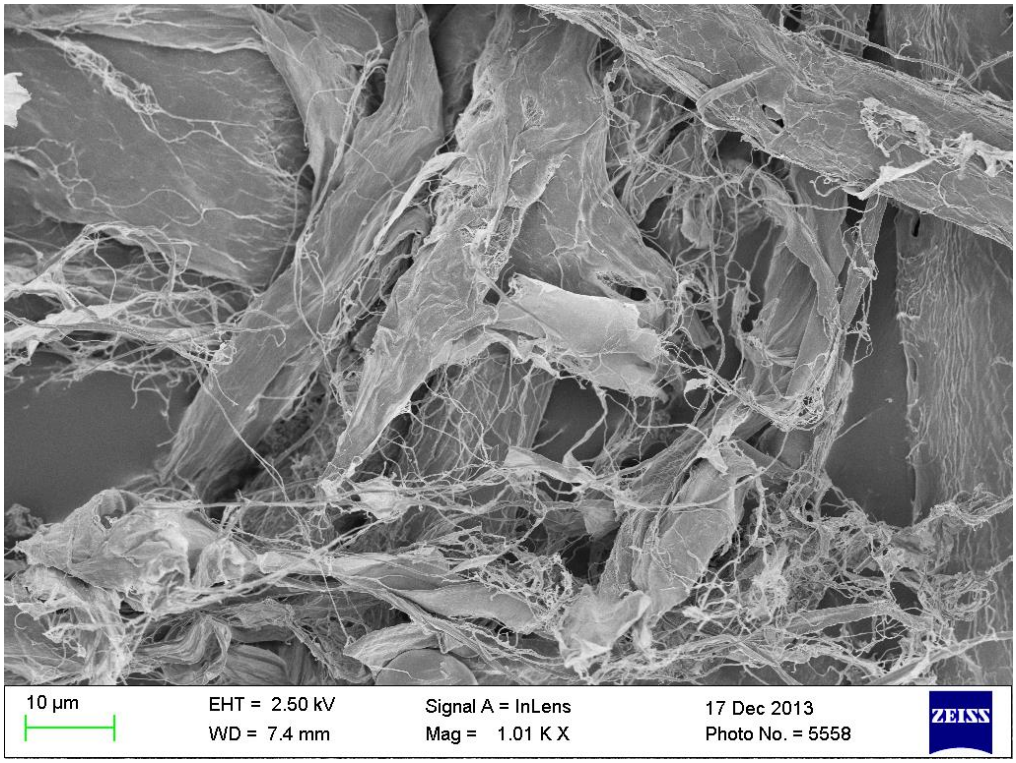
Optical microscope image of PAA treated, 60 minutes refined sample. Magnification of 20x.



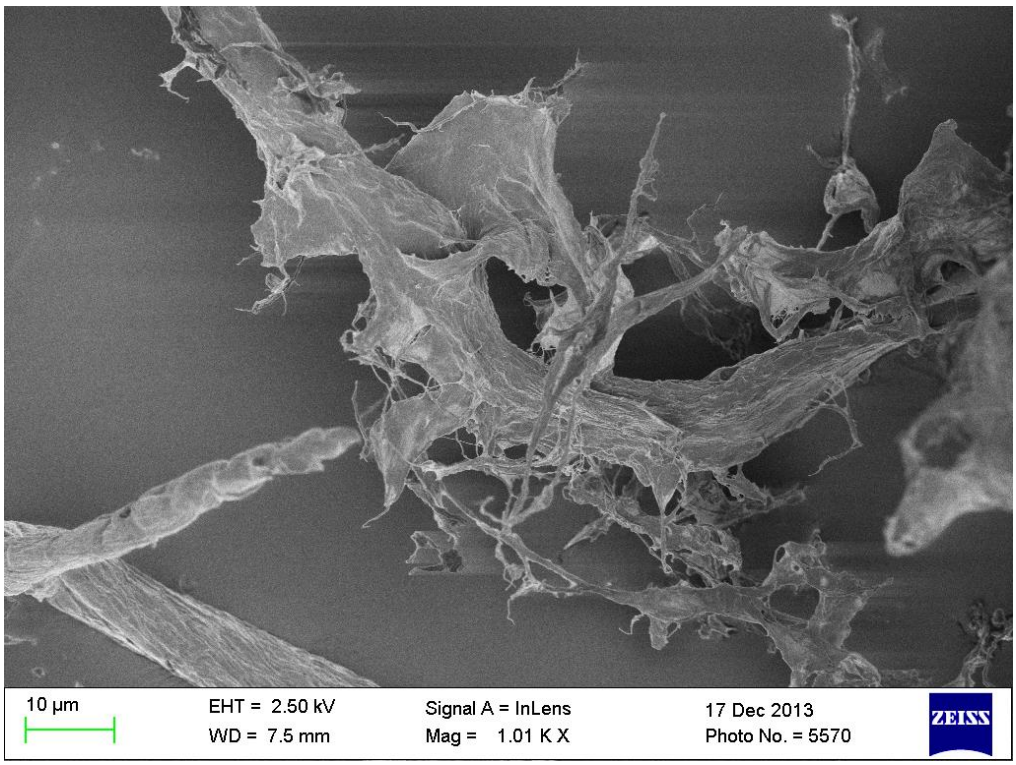
Optical microscope image of customized Valley beater, 60 minutes refined sample. Magnification of 20x.



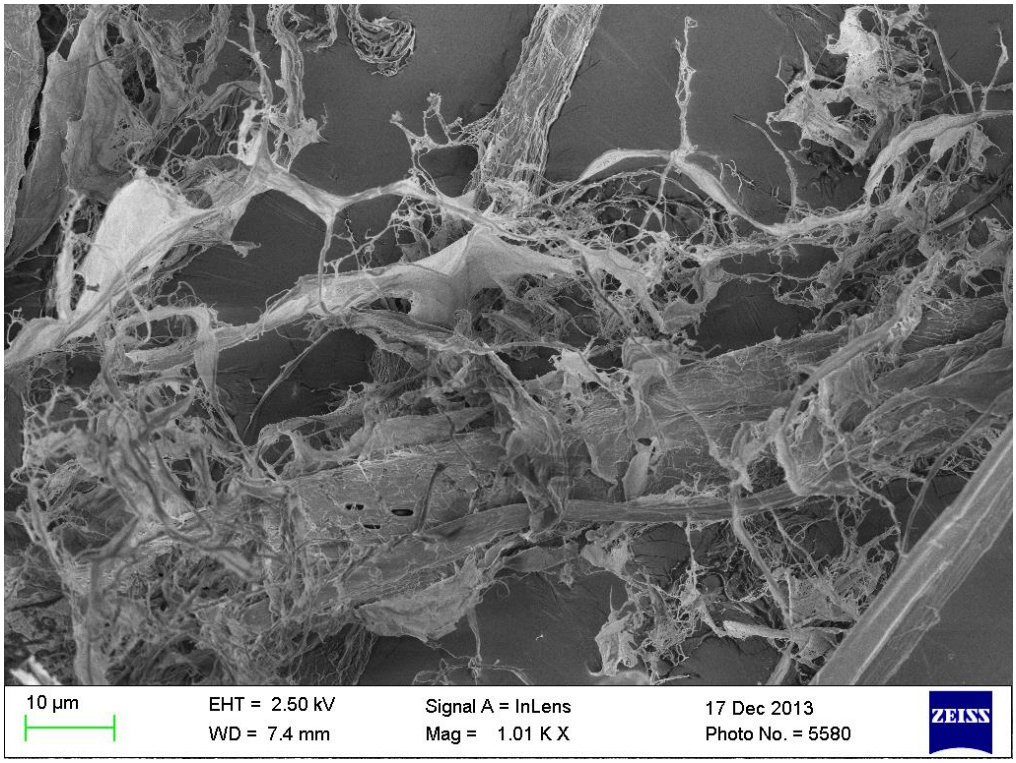
SEM image of reference, 30 minutes refined sample. Magnification of 1000x.



SEM image of cellulase treated, 30 minutes refined sample. Magnification of 1000x.



SEM image of PAA treated, 30 minutes refined sample. Magnification of 1000x.



SEM image of customized Valley beater, 30 minutes refined sample. Magnification of 1000x.